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Preparation and Reactions of Diels-Alder Adducts of Lignin-Derived Quinones

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PREPARATION AND REACTIONS OF DIELS-ALDER ADDUCTS OF LIGNIN-DERIVED QUINONES

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ABSTRACT

The goal of chemical pulping is to liberate the carbohydrate fibers from lignocellulosic materials, such as wood, through a delignification process. Pulping catalysts, such as anthraquinone, promote delignification rates such that lower cooking times and less severe conditions can be employed. As a result of their action, catalysts lead to improved selectivity, i.e., preferential degradation of lignin *versus* degradation of cellulose and other carbohydrates.

A disadvantage to the use of pulping catalysts is that they are relatively expensive and are lost during the pulping process. However, quinone structures can be generated from lignin through the use of several oxidative techniques. Modification of these quinones through Diels-Alder reactions with various dienes can enhance their stability and give them the characteristics needed to act as delignification catalysts.

Although significant catalytic activity is exhibited by naphthoquinone and phenanthrenequinone structures, these compounds do not achieve the high degree of activity demonstrated by anthraquinone. Pulping with an isomeric mixture of 2,6- and 2,7-dimethylanthraquinone, however, has shown that these compounds are superior to anthraquinone in terms of both reduction in kappa number and increase in yield.

The most promising synthetic pathway to the production of useful delignification catalysts, such as dimethylanthraquinone, appears to be a two-step approach in which lignin is first degraded into monomeric units, such as vanillin and syringaldehyde, and these smaller compounds are subsequently oxidized to methoxy- or 2,6-dimethoxy-*p*-benzoquinone.

Nearly quantitative yields of p-benzoquinones may be obtained from compounds containing benzylic hydroxyl groups through the use of potassium nitrosodisulfonate. Hydrogen peroxide is effective in generating p-benzoquinones and related hydroquinones from compounds containing α-carbonyl groups (up to 96% combined yield). Peracetic acid is an effective oxidant on compounds with either α-hydroxyl groups of α-carbonyl groups; up to a 93% combined yield of quinones and related compounds, which can be easily converted into quinones, may be obtained.

Potassium nitrosodisulfonate, peracetic acid, and electrochemical anodic oxidation have been used successfully to generate p-benzoquinones from lignin, but yields are often low. Highest yields (up to 16%) have been obtained with potassium nitrosodisulfonate.

Thus, lignin or simple phenolic compounds obtained from lignin may be oxidized to methoxy- or 2,6-dimethoxy-p-benzoquinones. These quinones may then be converted into anthraquinone compounds through Diels-Alder reactions using dienes such as isoprene. In the future this may result in the production of low-cost pulping accelerators which could lead to very cost-effective pulping processes.

PERSPECTIVE

The goal of chemical pulping is to liberate, without excessive degradation, carbohydrate fibers from lignocellulosic materials, such as wood, through a delignification process. For many delignification processes, such as the widely used kraft process on wood, the loss of carbohydrate material may be comparable to, or even exceed, the loss of lignin.

Most chemical pulping processes employed today involve heating the lignocellulosic material in water at temperatures near 170°C in the presence of alkali (NaOH, $NaHCO_3$, Na_2CO_3) with a pulping accelerator, such as Na_2S, Na_2SO_3, or anthraquinone (AQ). While lignocellulosic materials can be partially delignified by NaOH alone, the cooking times are excessively long and the cellulosic fibers are extensively degraded. The "accelerators" promote the delignification rates such that lower cooking times or less severe conditions can be employed, meaning that there is less carbohydrate fiber damage. In other words, the accelerators lead to improved selectivity, i.e., preferential degradation of lignin versus degradation of cellulose and other carbohydrates.

The penalty for improved selectivity often comes in the form of the cost of the added chemicals, process complexity, and environmental concerns. For example, the sulfur accelerators can produce odorous air emissions, require expensive chemical recovery equipment, and produce a dark pulp that is very difficult to bleach.

There are examples, however, of improved selectivity achieved without penalties. The soda/AQ pulping system should not possess the harmful air emissions exhibited by the sulfur processes. Also, the sulfur emission problems associated with the kraft and sulfite pulping systems can be lowered by employing

less sulfur chemicals and supplementing with AQ, i.e., the kraft/AQ and sulfite/AQ processes.

The popularity of the kraft pulping process stems from its adaptability to many different types of lignocellulosic sources, its ability to produce strong pulps, and its low chemical costs. Associated with this latter point, there is a chemical recovery system in place which concentrates and burns the pulping liquors; the molten salts from the recovery furnace are treated with water and causticized (to convert Na_2S to NaSH and NaOH, and Na_2CO_3 to NaOH) to provide the chemicals for the next pulping run. Chemical recovery is more difficult with the sulfite pulping process and is one of the major problems associated with the use of this process.

A sulfur-free pulping process such as soda/AQ, could lend itself to an easier, less energy-intensive chemical recovery system than that of the kraft process. In principle, a simple combustion scheme, such as DARS, which does not involve the reduction of sulfate in a molten salt environment, is possible.[1] However, in the soda/AQ pulping system, the chemical recovery leading to NaOH regeneration destroys the residual AQ in the pulping liquors. Also, considerable amounts of AQ are lost during the process of pulping. Therefore, AQ pulping processes have a nonreturnable chemical cost associated with them, namely the cost of the AQ. Even when used at a level of 0.1%, based on the weight of lignocellulosic material, the cost of AQ is an economic deterrent which has inhibited its widespread use.

Although there are only a few operating AQ mills in the U.S., on a world-wide basis more than 70 mills have continuously or intermittently used AQ pulping, and the number of mills that have conducted trials with AQ exceeds

100.[2] Because of the potential for increasing pulp yield and decreasing energy costs, the demand for AQ or other quinone pulping processes would almost certainly increase if the additives could be obtained at a reasonable cost. This thesis addresses producing quinone and related pulping accelerators from lignin and simple compounds related to lignin. Because the cost of lignin and related substances can be very low and product purification may not be necessary, low-cost pulping accelerators could be available. Such accelerators could lead to cost-effective pulping systems, having many desirable features.

At the present time, lignin by-products formed during pulping are generally not isolated but instead are burned during the chemical recovery cycle. The heat released from their burning is used to generate energy, generally superheated steam. The value of the lignin depends on the cost of alternative fuels; in October of 1987 its value was estimated to be 3.6 cents per pound. Thus, lignin and its by-products are low-cost, plentiful substances for possible conversion into valuable organic chemicals.

THESIS OBJECTIVES

This thesis has two objectives: (1) the generation of quinones from lignin-related compounds, the enhancement of the ring structures of these quinones through the use of Diels-Alder reactions, and the testing of the resulting compounds for activity as pulping catalysts; (2) the application of the information gained in satisfying the first objective toward the production of a pulping catalyst from lignin.

By satisfying these objectives, it is hoped that the groundwork will be laid for an industrial process in which low-cost pulping accelerators can be generated from the lignin by-product of a pulping reaction.

BACKGROUND

CHARACTERISTICS OF QUINONE PULPING CATALYSTS

The mechanisms by which delignification catalysts function are not known with certainty.[3] For the most widely known catalyst, AQ, it has generally been accepted that both AQ and anthrahydroquinone (AHQ), a reduced form of AQ, play important roles during pulping. The redox cycle shown in Fig. 1 explains the catalytic activity of AQ, the high pulp yields, and the fast delignification rates. In reducing AQ to AHQ, carbohydrate end groups are oxidized and stabilized toward degradation reactions. Lignin is degraded and solubilized as it is reduced and oxidizes AHQ back to AQ.

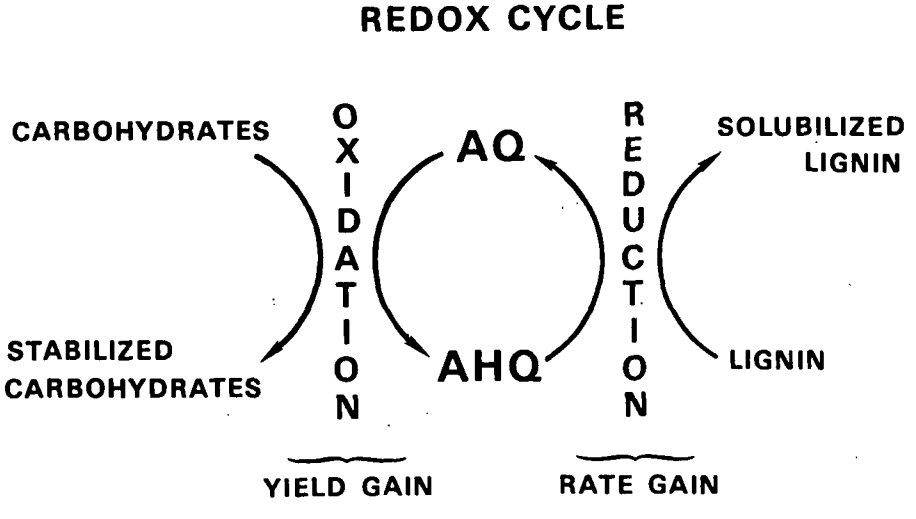


Figure 1. A redox cycle proposed for explaining the catalytic action of anthraquinone.

Even without knowing the exact nature of the mechanisms by which catalysts act, it is still possible to examine the compounds themselves and determine what features they have in common which contribute to their effect. Initial work done by Holton[4] showed that quinone compounds in general were effective pulping

additives. An interesting, but unexplained, finding was that benzoquinones produced negative results. However, naphthoquinones were found to be slightly effective, and anthraquinones were very effective. Furthermore, Holton showed that electron-withdrawing groups such as sulfonate groups seemed to reduce an additive's effect while electron-donating groups were found to enhance an additive's effect.

A group at Ciba-Geigy Corporation, headed by D. Werthemann,[5] has performed exhaustive studies into the structural features needed for good pulping catalytic activity. They have measured the half-wave potentials of about 50 pulping additives at 90°C in 1N NaOH in the presence of wood and concluded that a redox catalyst requires a reduction potential in the range from -0.55 to -1.05 V vs. a saturated calomel electrode (SCE).

In a study of several diaryl ketones, Eckert and Amos[6] found no correlation between reduction potential and pulping catalytic activity. All of the inactive compounds, however, were reduced at potentials more negative than -1.2 V vs. SCE.

Compounds which have a low normal potential will not be easily reduced, and thus the portion of the redox cycle mechanism involving carbohydrates may not exist. Once in the reduced form, however, they can be very active in promoting delignification. Quinones are somewhat easily reduced because there is a gain in resonance energy associated with the hydroquinone form. Compounds which have a high gain in resonance energy upon reduction, on the other hand, have a high normal potential. These compounds are also not as effective as compounds such as AQ which have a lower gain in resonance energy and, hence, a lower normal potential.

In general, as the number of rings in quinone compounds increases, the normal potential decreases and catalytic activity increases. As the gain in resonance energy decreases, however, it is more difficult to reduce a compound, and the reduced form will be less stable. The optimum ring structure for catalyzing delignification seems to coincide with that of anthraquinone. The introduction of electron-releasing groups will tend to lower the normal potential and therefore somewhat increase the rate of delignification.

Lindenfors[7] pointed out that since it is the reduced form of an additive that is active in promoting the rate of delignification, those compounds which are the most effective reducing agents (when in the reduced form) should also be the most effective catalysts. Lindenfors also pointed out, however, that a good correlation cannot be expected between the reduction in kappa number obtained under the severity of alkaline conditions and normal potential determined under specified, idealized, conditions.

Werthemann[8] examined the influence of solubility on the delignification efficacy of various quinone additives. In order for an additive to interact with the wood, it must be soluble in the pulping solvent (generally water). The lower efficacy of 2-ethylanthraquinone as compared to 2-methylanthraquinone was explained in terms of the latter's greater solubility in water. For maximum effectiveness, the optimum solubility for quinone pulping additives was found to be 0.4 ± 0.1 mg/L in 1N NaOH at room temperature.

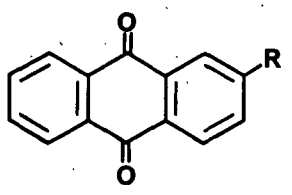
The solubility of neutral quinones in 1N NaOH at room temperature probably also reflects upon the solubility of the reduced hydroquinone ions and ion radicals at pulping temperatures. It seems likely that the solubility of the ions would be equal to or more important to the catalytic action than the solubility

of neutral additives. If the additive structure is quite different than the ones tested by Werthemann, the 0.4 ± 0.1 mg/L solubility may not be applicable.

Variations in the effectiveness of several additives have been explained in terms of a balance between xylophilicity (affinity for wood) vs. hydrophilicity (affinity for water).[9] The relatively low efficacy of anthraquinone-2-sulfonate, for example, is attributed to the hydrophilic preference for the liquid phase as opposed to the unreacted lignin in the wood phase. On the other hand, a greater wood adsorption, promoted by the methyl group, would explain the increased efficacy of 2-methylanthraquinone as compared to AQ. For some additives, however, this concept does not appear to apply. For example, the xylophilicity/hydrophilicity balance cannot explain the poor performance of 2-hydroxyanthraquinone. It is also worth pointing out that solubility and the xylophilicity/hydrophilicity balance counteract each other to a certain extent. If very high solubility leads to lower affinity for wood, an additive's effect may be diminished.

Work done by Eckert and Amos[10] supports the data obtained by Werthemann. Eckert and Amos studied the efficacies of several derivatives of AQ in which the hydrophilicity was varied by altering the substituent at the 2-position. Compounds used in the study are shown in Fig. 2; included in the figure are polarographic peak potentials obtained in an alkaline system.

Regardless of the redox potential, carboxyl groups strongly diminish the activity of AQ in soda pulping, probably because of the increased hydrophilicity of the carboxyl derivatives. Nonpolar hydrocarbon side chains, on the other hand, tend to increase the activity of AQ. This suggests that adsorption phenomena may play a strong role in additive performance. The adsorption effects could greatly magnify the working concentration of an additive beyond its calculated concentration in the bulk liquor.



R Group	Polarographic Peak Potential (V vs. SCE)[a]
-H	-0.680
-COOH	-0.656
$-CH_2CH_2COOH$	-0.720
-CH=CHCOOH	-0.627, -0.715
$-CH_2CH_2CH_2OH$	-0.717
$-CH_2CH_2CH=C(CH_3)_2$	-0.725

[a]Potentials obtained in 0.5N NaOH/0.1N NaCl in 50% aq. DMF.

Figure 2. Polarographic peak potentials of selected compounds used in hydrophilicity studies.[10]

In addition to the factors already considered, the fact that an additive must survive the severe conditions of chemical pulping cannot be overlooked. Several researchers have pointed out that even if all other factors are favorable, a high temperature alkaline environment can completely destroy a compound before it has a chance to work.[6,7,11,12]

In a study of roughly 300 pulping additives, Donnini, et al.[13] found that redox potential, solubility, xylophilicity/hydrophilicity ratio, chemical stability, and structure, or a combination of these factors are important in determining the catalytic enhancement of delignification. In some cases steric hindrance may come into play. Amos and Eckert[14] used this concept to explain the superior effect of 2,3-dimethylanthraquinone as compared to 1,4-dimethylanthraquinone.

In summary, stability under pulping conditions is of key importance for a pulping catalyst. Most effective compounds contain a quinone type structure. A reduction potential of -0.5 to -1.1 V vs. SCE and a solubility of approximately 0.4 mg/L in 1N NaOH also appear to be important, as well as an appropriate xylophilicity/hydrophilicity balance.

CONVERSION OF LIGNIN AND LIGNIN-RELATED COMPOUNDS TO QUINONES

Lignin and degraded lignin, such as may be found in a spent pulping liquor, consists of phenolic and etherified phenolic units with generally one or two methoxyl groups adjacent to the phenolic hydroxyl group, and an alkyl side chain para to the phenolic hydroxyl group.[15] As shown in Fig. 3, oxidation of the phenolic hydroxyl group and an adjacent methoxyl group can convert a lignin unit to an o-benzoquinone. Oxidation of the phenolic hydroxyl group together with oxidative degradation of the p-alkyl side chain can convert a lignin unit into a p-benzoquinone.

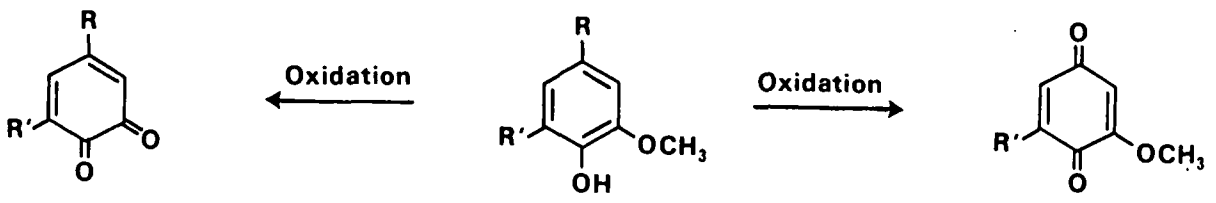


Figure 3. Oxidation of a lignin unit to quinone structures.

There have been numerous oxidative techniques that have been applied to lignin and lignin-related materials; often these result in the generation of o- or p-benzoquinones or related compounds. Many of the techniques that have been reported in the literature are discussed below.

Thermal/Chemical Modifications

In an attempt to produce catechol structures which could be subsequently oxidized to o-quinones, Furman[16] heated kraft lignin dissolved in 0.1N NaOH at 250°C. After this treatment, the lignin was acetylated and analyzed by proton NMR. It was clear from the spectral data that the lignin was increasingly demethylated as the heating time was increased.

By employing reductive acetylation procedures, Furman was able to establish that there was an increase in quinone structures with the thermal treatment. Apparently some of the catechol structures which resulted from the demethylation were oxidized to quinones. Infrared and UV spectral analysis indicated that while demethylation was clearly occurring, the lignin was also undergoing some condensation reactions.

Upon heating hydrolysis lignin in aqueous solutions of sodium sulfide at temperatures above 220°C, Prokshin and Bogomolov[17] found that a condensation process took place which produced structures of the phenanthrene type by cyclization of stilbene derivatives of lignin. Chemical and spectral analysis indicated a higher content of hydroxyl, carboxyl, and carbonyl groups as compared to the original lignin. The carbonyl group content was found to be 2.33 meq/g and was assumed to be mainly of the quinone type.[18]

Nadein, Prokshin, and Bogomolov[19] found that a high content of quinone and catechol structures were produced when kraft lignin was heated in white liquor at 240-320°C. It was found that the formation of these structures increased as the degree of demethylation increased. A maximum content of 2.67 meq/g of carbonyl groups was found; reduction with sodium dithionite indicated that up to 1.95 meq/g of quinone groups, mainly of the o-quinone type, were present. The

formation of quinone structures was further supported by differential UV spectral evidence.

Together with the easily oxidized catechol structures, the quinone groups represent an oxidation/reduction system typical of most delignification catalysts. Prokshin, Nadein, and Bogomolov[20] tested the products obtained as additives in alkaline pulping. The addition of 1.0% of the demethylated lignin (based on oven dry chips) was found to increase the yield of both kraft and soda pulp by approximately 2%, and the kappa number was found to be slightly lowered. The effectiveness of the additive increased with increasing degree of demethylation.

Recent work has confirmed the beneficial effect of using demethylated lignin as a pulping additive at addition levels of 1-2%.[21,22] Analytical work has indicated that the demethylated lignin is a polydisperse product composed of condensed quinone structures, probably resulting from a combination of the initial lignin and low-molecular-weight degradation products.[23]

Chemical Modifications

Potassium Nitrosodisulfonate (Fremy's Salt)

Potassium nitrosodisulfonate, Fremy's salt [$\cdot ON(SO_3K)_2$], has been used in the preparation of both o- and p-benzoquinones through the oxidation of phenols.[24] A mechanism for the reaction is presented in Fig. 4. In general, the oxidation of a phenol with a free para position results in a p-quinone; if the para position is blocked, an o-quinone is usually produced.

Adler and Lundquist[25] examined the reactions of Fremy's salt with guaiacyl lignin model compounds and developed a procedure to determine the number of phenolic units in softwood lignin which had free 5-positions. They observed that model compounds which contained an α-carbonyl group did not react. Those

compounds which contained an α-hydroxyl group, however, were reactive; in these cases oxidation led to cleavage of the side chains and the production of p-quinones.

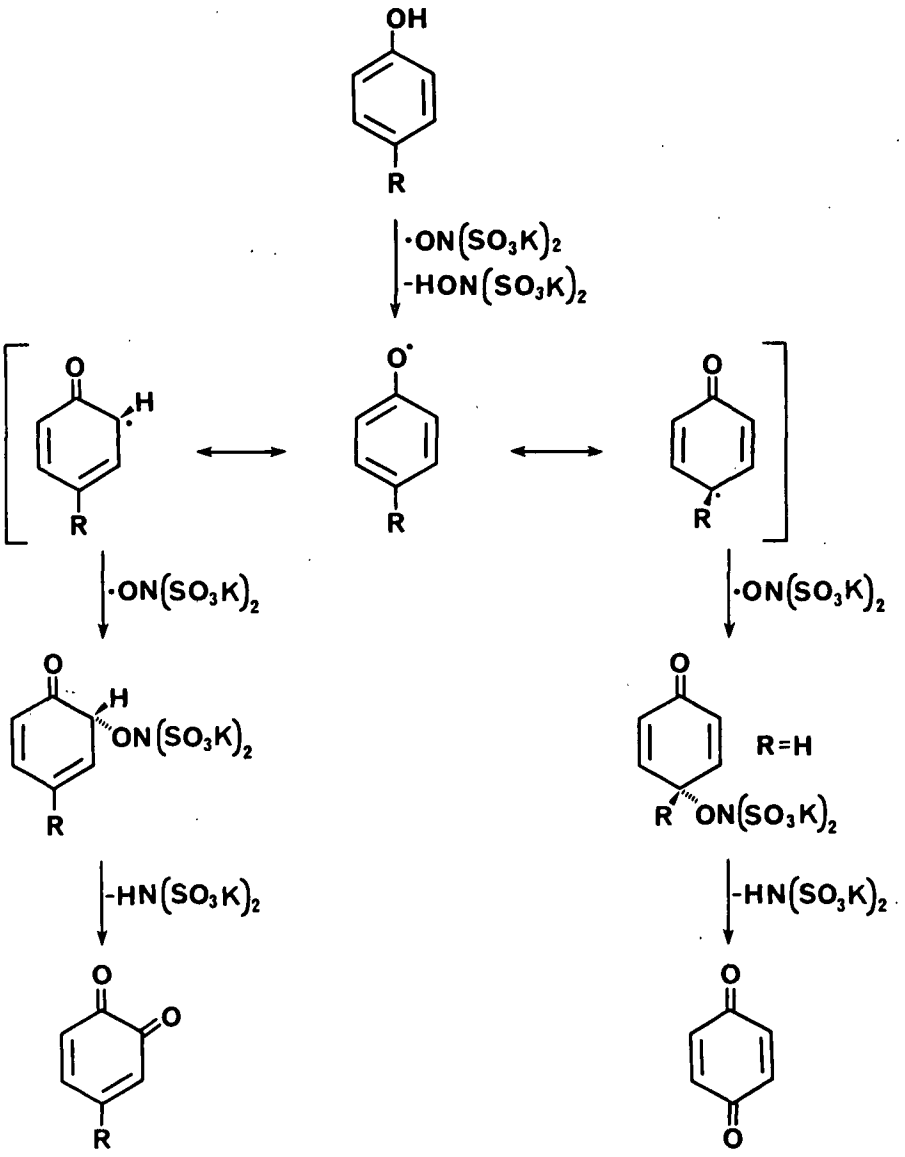


Figure 4. Fremy's salt oxidation of phenols.[24]

Recent work has shown that Fremy's salt can be used to generate p-benzoquinones from several p-hydroxybenzylalcohols, p hydroxybenzoic acids, and p-hydroxybenzaldehydes.[26,27] High yields were obtained from vanillic acid, syringic acid, and syringaldehyde; vanillin was not converted. A mechanism for the reaction of p-hydroxybenzoic acids is presented in Fig. 5.

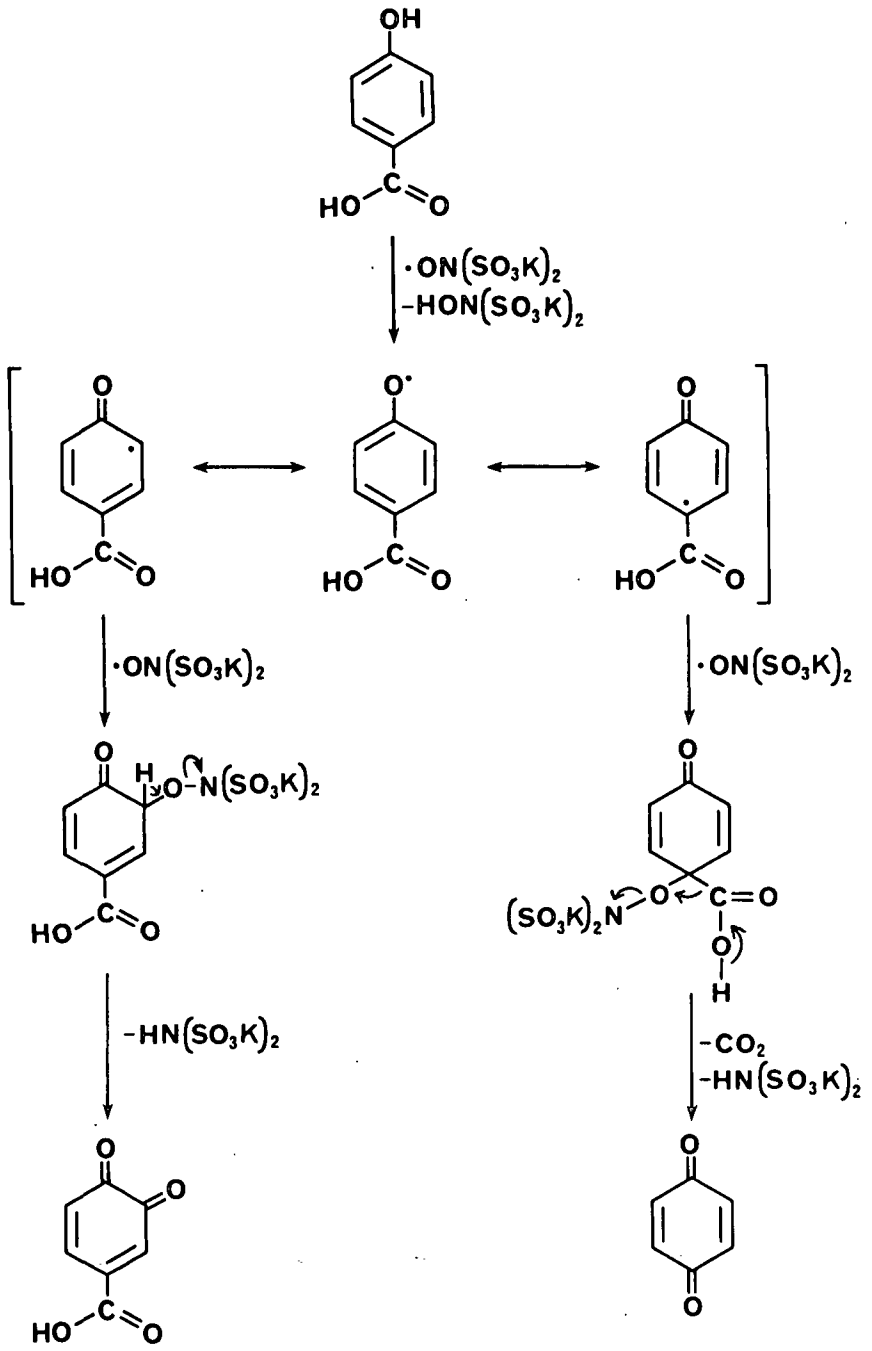


Figure 5. Fremy's salt oxidation of p-hydroxybenzoic acids.[27]

Sodium Periodate

Both o- and p-quinones can often be obtained by direct oxidation of phenyl ether compounds. A useful method for converting catechol monoethers into o-quinones utilized sodium periodate.[28] As shown in Fig. 6, the reaction is

regarded as a nucleophilic attack by water on a periodate ester to give a hemiketal which then yields the quinone. Condensation reactions of initially formed o-benzoquinones often lead to o-naphthoquinones.[29,30]

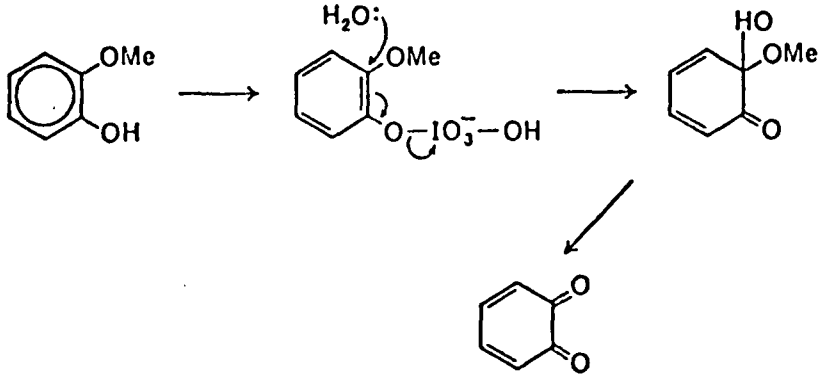


Figure 6. Oxidation of guaiacol using sodium periodate.[28]

Adler and Hernestam[31] have examined the reactions of sodium periodate in work with many guaiacyl lignin model compounds. Excess periodate was shown to cause further oxidation of o-quinones to produce dicarboxylic acids. Adler, Hernestam, and Walldén[32] used periodate oxidation on Brauns and Björkman lignin preparations. Furman[33] was able to demethylate lignin with sodium periodate to produce o-quinone structures. The degree of demethylation, with subsequent quinone formation, could be effectively varied by changing the time of reaction.

Hydrogen Peroxide

Several researchers have studied the effect of alkaline hydrogen peroxide on lignin and lignin model compounds. Reeves and Pearl[34] found that softwood lignin model compounds containing α-carbonyl groups were reactive when a free hydroxyl group was present in the position para to the side chain. Under these conditions the side chain was cleaved to yield methoxyhydroquinone. A proposed mechanism for the formation of the anionic form of the hydroquinone is shown in Fig. 7.

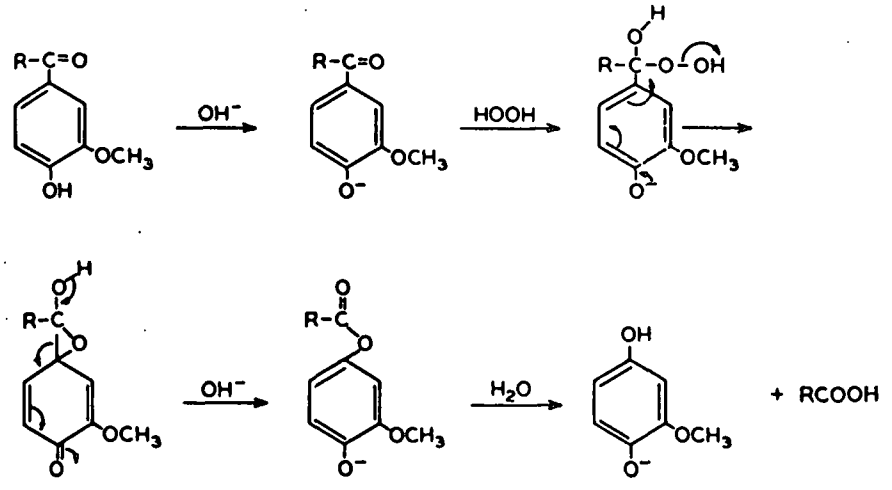


Figure 7. Hydrogen peroxide oxidation of lignin units containing α-carbonyl groups.[34]

Model compounds containing α,β-unsaturated aldehydes and β-carbonyl groups were converted to benzaldehydes.[34] Other potentially oxidizable functional groups such as ring-conjugated double bonds, phenolic and primary alcohol groups, and aliphatic and phenolic ether linkages were not attacked.

Bailey and Dence[35] examined the hydrogen peroxide oxidation of softwood lignin model compounds as well as softwood lignin itself. Creosol was initially oxidized to 4-methyl-o-benzoquinone; final products included oxalic, acetic, methylmaleic, and methylfumaric acids. A small amount of the corresponding o-quinone was initially obtained from the reaction of α-methylvanillyl alcohol; methoxy-p-benzoquinone was also identified. These intermediate products were then degraded to a mixture of maleic, malonic, oxalic, oxalacetic, and methoxy- or hydroxysuccinic acids. Oxidation of spruce groundwood lignin resulted in the recovery of the same acids.

Using similar reaction conditions, Kempf and Dence[36] studied the reactions of the syringyl analogs of creosol and α-methylvanillyl alcohol, 4-methylsyringol

and α-methylsyringyl alcohol. It was again found that the initially formed o- and p-quinone intermediates were subsequently oxidized to low-molecular-weight dicarboxylic acids. A mechanism for the secondary oxidative cleavage of quinones has been proposed by Gellerstedt[37] and is presented in Fig. 8.

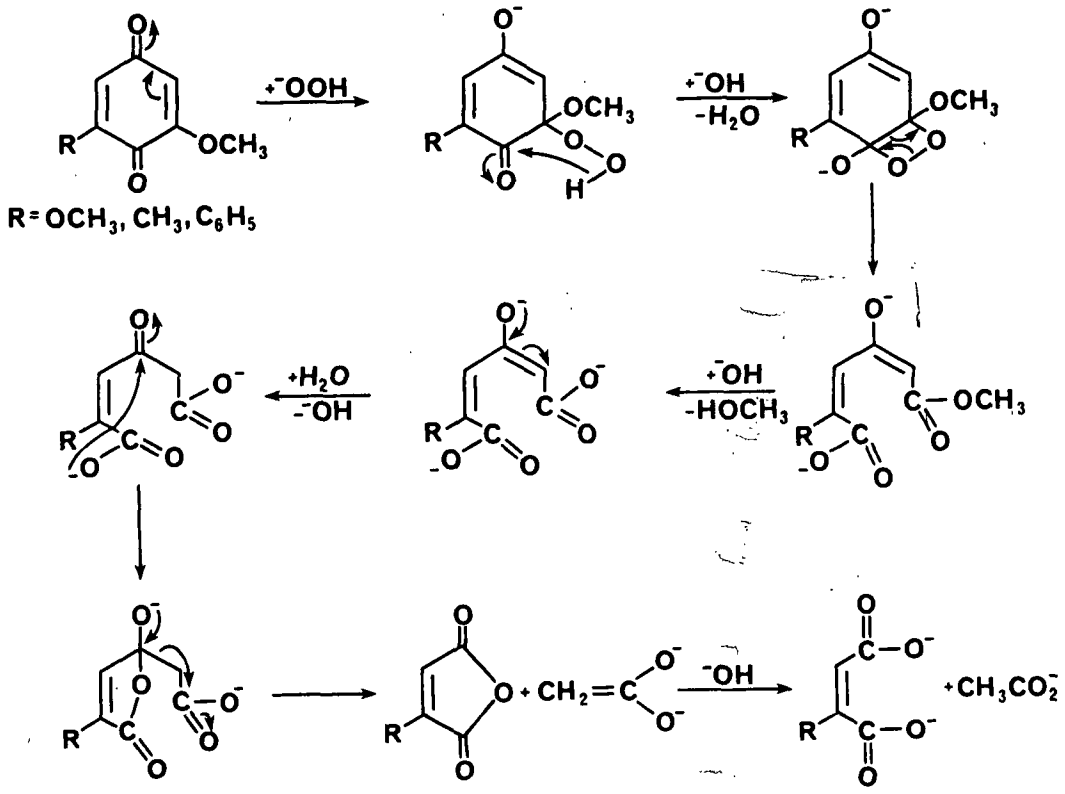


Figure 8. The hydrogen peroxide degradation of quinones.[37]

In general, syringyl model compounds have been found to react more readily with peroxide than guaiacyl models. With both models, unetherified phenolic rings seem to be necessary for reaction to occur.[35,36,38]

Peracetic Acid

The peracetic acid oxidation of both lignin and lignin model compounds has been studied by several researchers. Strumila and Rapson[39] investigated the oxidation of acetovanillone, α-methylvanillyl alcohol, vanillyl alcohol, and vanillin under neutral conditions. Oxidation occurred primarily at the side

chain para to the phenolic hydroxyl group. Vanillyl alcohol and vanillin yielded only vanillic acid. In the cases of acetovanillone and α-methylvanillyl alcohol, however, complex mixtures of aliphatic dibasic acids were obtained; 4-acetoxy-2-methoxyphenol was identified as a reaction intermediate.

Nimz and Schwind[40] oxidized eight monomeric lignin model compounds with peracetic acid at pH 3. Compounds containing α-carbonyl groups were found to react easily, yielding relatively high amounts of methoxyhydroquinone monoesters, methoxyhydroquinones, and methoxy-p-benzoquinones. The reaction of vanillin resulted in a 12% yield of methoxy-p-benzoquinone and a 21% yield of methoxyhydroquinone. The yield of 2,6-dimethoxy-p-benzoquinone from syringaldehyde was claimed to be 82%. Acetovanillone yielded 5% methoxyhydroquinone. The reaction of α-hydroxyl compounds was much slower than that of α-carbonyl compounds. Neither methoxy-p-benzoquinone nor methoxyhydroquinone was obtained from either vanillyl alcohol or α-methylvanillyl alcohol.

Ishikawa, Oki, and Ohkubo[41] obtained high (around 50%) yields of methoxyhydroquinone in the peracetic acid oxidation of vanillin and acetovanillone. Neither methoxyhydroquinone nor methoxy-p-benzoquinone were obtained from either α-methylvanillyl alcohol or vanillic acid, but a small amount of methoxyhydroquinone was obtained from vanillyl alcohol. The oxidation of dimeric lignin model compounds containing α-hydroxyl groups by these same researchers[42] was found to result in the production of slight amounts of methoxy-p-benzoquinone and methoxyhydroquinone.

Other researchers, however, using similar reaction conditions on other lignin model compounds and lignin itself, have not reported the generation of measurable amounts of quinones or hydroquinones.[40,43-45] Model compounds which

do not contain an oxygen function at the α-position are generally unreactive or, if harsher reaction conditions are employed, yield complex mixtures of carboxylic acids.

Several researchers[39-41] have proposed that the peracetic acid oxidation of guaiacyl lignin model compounds containing α-carbonyl groups proceeds via a Baeyer-Villiger rearrangement to form esters which upon hydrolysis produce methoxyhydroquinones. The hydroquinones may be further oxidized to quinones, or they may be degraded into smaller carboxylic acids. As shown in Fig. 9, compounds containing α-hydroxyl groups are first oxidized to the corresponding α-carbonyl compounds.

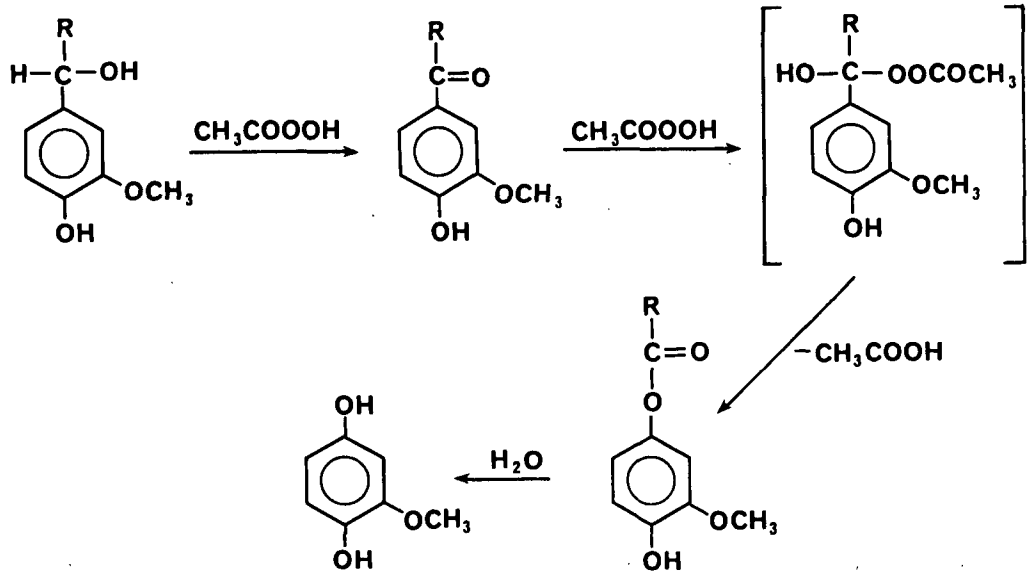


Figure 9. Peracetic acid oxidation of lignin model compounds.[41]

Other Chemical Reactions

Silver (II) oxide was used by Snyder and Rapoport[46] to demethylate naphthohydroquinone and benzohydroquinone dimethyl ethers. Functional groups such as

alcohols, aldehydes, ketones, and olefins were not affected by the reaction. If this procedure worked when applied to lignin, the resulting catechol structures might act as the reduced form of a delignification catalyst. Other chemical oxidative techniques reported to generate quinones from lignin-related compounds include the use of chlorous acid,[47] hydrogen peroxide/sodium hypochlorite,[48] and 2,3-dichloro-5,6-dicyanobenzoquinone.[49]

Chudakov, et al.[50] studied quinone formation from hydrolysis lignin by oxidation with Mn^{+3} in hydrochloric and sulfuric acid, hydrogen peroxide in hydrochloric and sulfuric acid, and atmospheric oxygen in alkaline solution at 150-160°C. Infrared spectroscopy was used to indicate the increase in quinone carbonyl groups. When added to kraft pulping liquor in amounts of 3% based on oven-dry wood, the air-oxidized lignin had a beneficial effect on the yield and mechanical strength of the pulp.

Extended quinone structures (diphenoquinones) may be formed by processes involving oxidation, coupling, and further oxidation.[51] This reaction sequence is shown in Fig. 10, where the substituent para to the hydroxyl group is hydrogen.

Para substituents other than hydrogen may also be eliminated in the course of the diphenoquinone formation. Best results have been found when oxidation has been effected with ferric chloride, alkaline ferricyanide, silver oxide, and lead dioxide. Stable aroxyl radicals, isopentyl nitrite, transition metal complexes, oxygen in alkaline solution, and silver carbonate/Celite have also been used.[51]

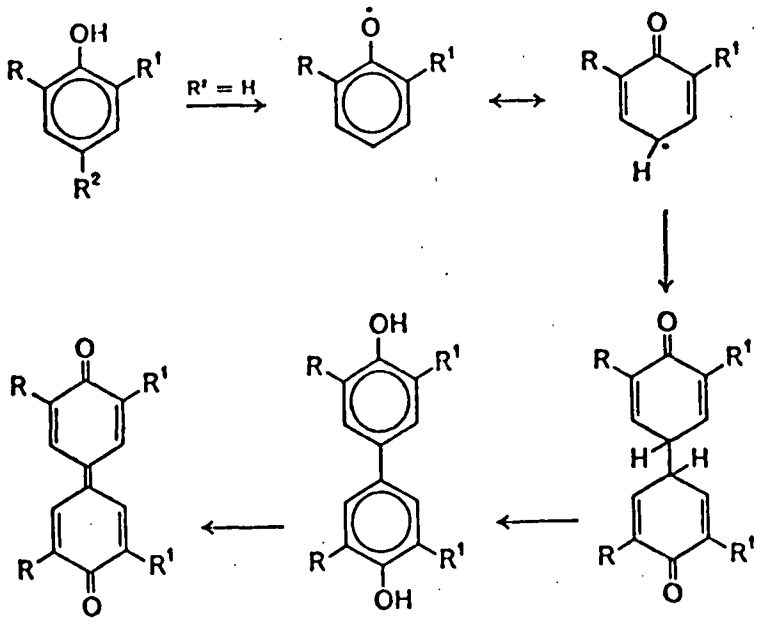


Figure 10. Formation of extended quinone structures through oxidation and coupling.[51]

Although oxidative reactions of lignin phenolic units often lead to quinone structures, alternative reactions are possible. An oxygen function in the benzylic position of an arylalkane, for example, greatly enhances the rate of hydride ion abstraction by quinones from this position to produce aldehydes and ketones.[52]

The addition of either molecular oxygen or hydrogen peroxide to an alkaline lignin solution can be used to produce quinones; however, the use of excess reactant can result in quinone degradation to dibasic acids and carbon dioxide.[53] Quinones initially produced may be more reactive than the starting material.[36] The quinones may also react through several photochemical reactions.[54,55]

As shown in Fig. 11, in aqueous alkali benzylic acid rearrangements of hydroxyquinones, leading to carboxylic acids, are possible.[56] The rearrangements

of hydroxybenzoquinones appear to be more complex and lead to the production of dicarboxylic acids and carbon dioxide. Both hydroxybenzoquinones and hydroxynaphthoquinones tend to undergo ring-opening or ring-contraction reactions.[56,57] The cleavage of carbon-carbon double bonds occurs most readily when substituents cause the bond to be highly polarized. Treatment with alkali causes many benzoquinones to undergo complex reactions resulting in the formation of hydroquinols and amorphous polymeric materials.[57,58]

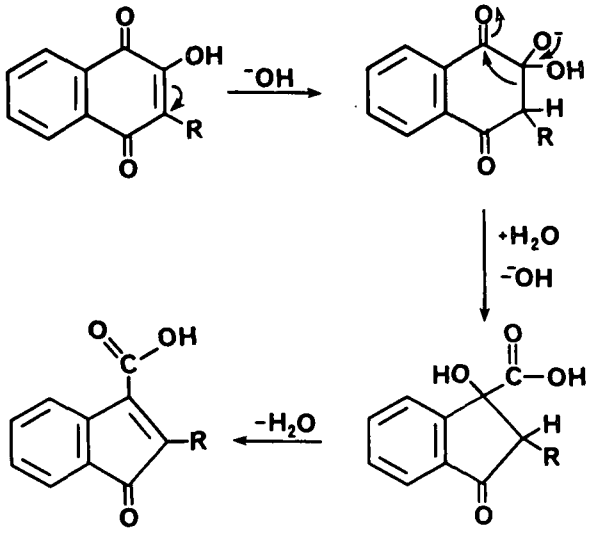


Figure 11. Benzylic acid rearrangement of a hydroxyquinone.[56]

Summary

It is clear that there are a number of chemical oxidative techniques that can be used to generate quinones from lignin and lignin-related compounds. Some, such as Fremy's salt and sodium periodate, may be useful in generating o-quinone structures, while others such as hydrogen peroxide and peracetic acid may be more prone to generate p-quinones. Reaction conditions and substrate structural characteristics, of course, play major roles in determining what products are obtained. The presence of a benzylic hydroxyl group, for example, permits the use of Fremy's salt for the generation of p-quinones rather than

o-quinones. Hydrogen peroxide appears to be more effective on compounds containing α-carbonyl groups. Peracetic acid may convert compounds containing either α-hydroxyl or α-carbonyl groups to p-benzoquinones.

For application in an industrial process, the cost and availability of a potential oxidant must also be kept in mind. From this standpoint, hydrogen peroxide or peracetic acid may be good choices. The challenge is to find appropriate reaction conditions which allow for maximum conversion of the substrate material into the desired quinones without the occurrence of the degradative reactions discussed above.

Electrochemical Modifications

The first steps in the anodic oxidation of phenolic compounds are generally believed to involve radical generation as shown in Fig. 12.[59] Under acidic conditions, the transfer of the second electron may occur more readily than the first; in this case the reaction product may be a dienone or a product derived from a dienone. Under basic conditions, the potential for the oxidation of the phenoxide radical may be much more positive than the potential for the oxidation of the phenolate ion. In this case there may be only a single electron transfer, and the phenoxy radicals generated may couple to form dimeric products.

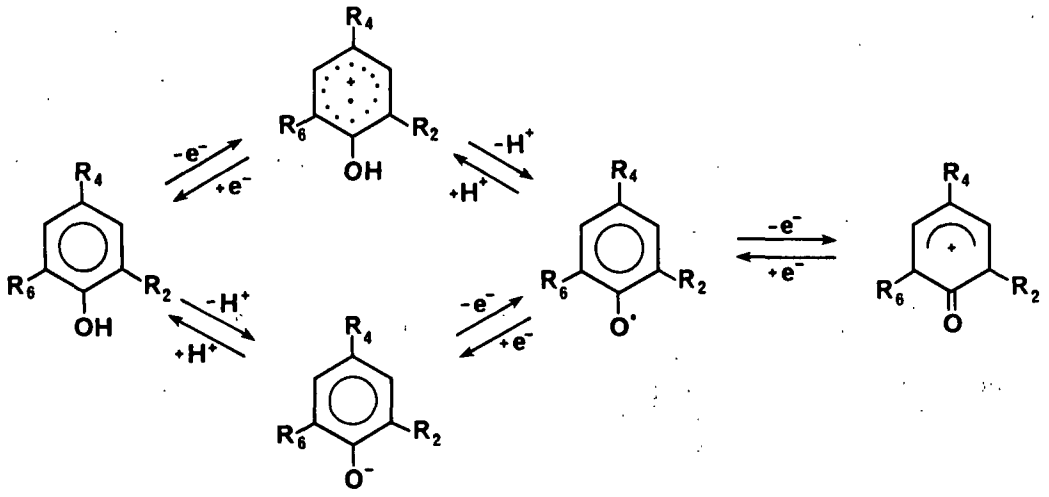


Figure 12. Electrochemical oxidation of phenolic compounds.59

Electrochemical oxidation has been applied to phenols, lignin model compounds, and to lignin itself. Quantitative conversion of 2,6-dimethylphenol into 2,6-dimethyl-p-benzoquinone, for example, can be achieved by anodic oxidation in sulfuric acid using a lead dioxide electrode or in aqueous acetonitrile using a platinum electrode.[51] The reaction is considered to proceed by way of an aroxyl radical, followed by conversion to a cation, and finally by a solvolysis. The reaction of the cation is shown in Fig. 13.

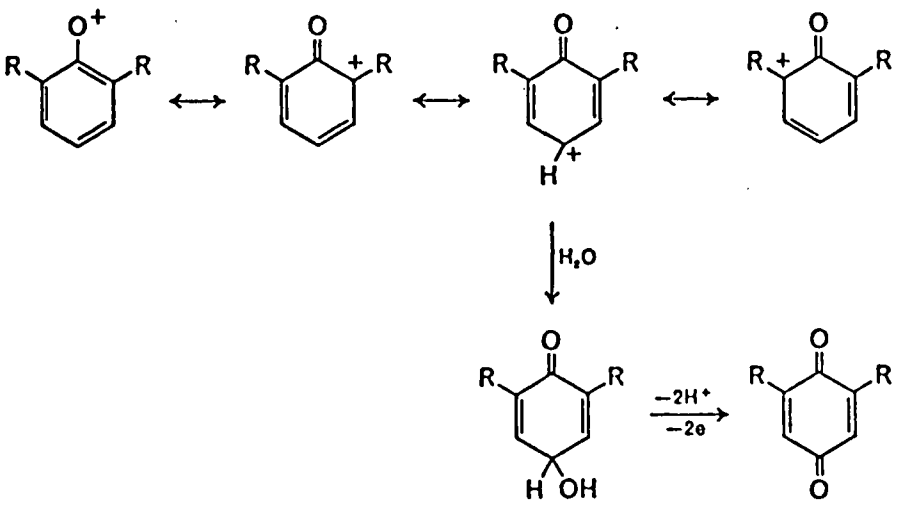
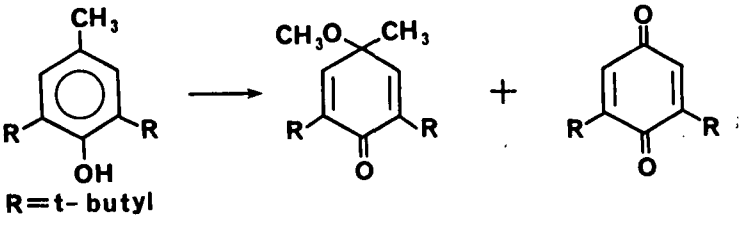


Figure 13. Electrochemical oxidation of 2,6-dialkylphenols.[51]

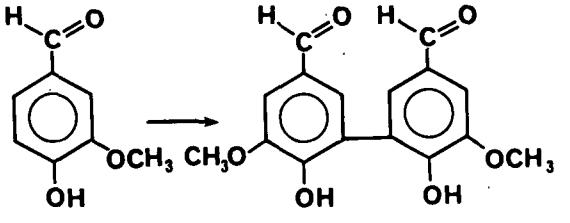
These processes were demonstrated in one of the first systematic studies of anodic oxidations of phenols, conducted by Vermillion and Pearl.[60] As shown in Eq. (1), the oxidation of 2,6-di-t-butyl-p-cresol in acetonitrile containing methanol resulted in a 65% yield of 2,6-di-t-butyl-4-methoxy-4-methylcyclohexa-2,5-dienone and a 10% yield of 2,6-di-t-butyl-p-benzoquinone. The oxidation of vanillin in acetonitrile under basic conditions gave dehydrodivanillin in 65% yield [Eq. (2)].

Ronlán and Parker[61] studied the oxidation of several trialkyl substituted phenols in acetonitrile and methylene chloride [Eq. (3)]. In the presence of

water, anodic hydroxylation occurred to give high yields of the corresponding 4-hydroxycyclohexa-2,5-dienones. Treatment of the 2,4,6-tri-t-butyl product with trifluoroacetic acid permitted quantitative conversion to the hydroquinone.



(1)



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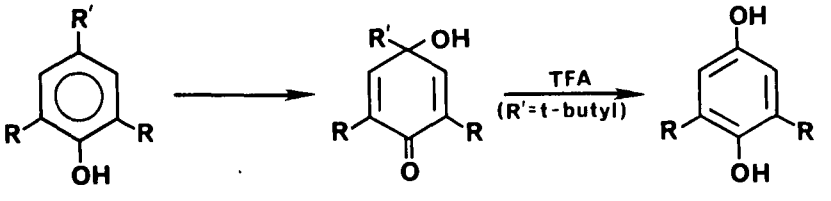


(3)

In a study of the oxidation of simple monohydric phenols at a lead dioxide anode in aqueous sulfuric acid, Nilsson, Ronlán, and Parker[62] also found that a hydroxyl group readily entered the 4-position. It was observed that 4-substituted phenols gave 4-substituted-4-hydroxycyclohexa-2,5-dienones; phenols without substituents at the 4-position were converted to p-benzoquinones.

Phenols substituted with alkoxy groups are more easily oxidized than the corresponding unsubstituted compounds.[59] Oxidation of p-methoxyphenol in the presence of water gives p-benzoquinone. Oxidation of 4-allyl-2-methoxyphenol in

methanol results in the four products shown in Fig. 14. The product at the lower right results from a Diels-Alder coupling reaction.

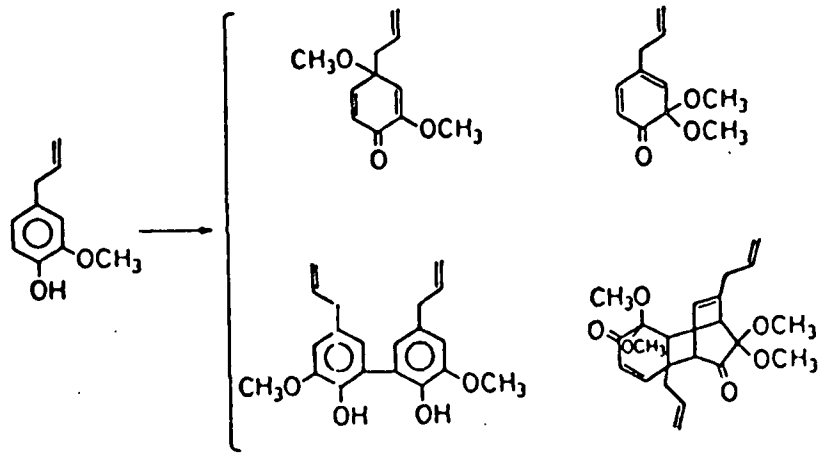


Figure 14. Oxidation of 4-allyl-2-methoxyphenol.[59]

As shown in Fig. 15, oxidation of 2,6-dimethoxy-4-allylphenol in methanol under neutral or slightly alkaline conditions results in two products, one of which is again a Diels-Alder adduct. The product of the reaction was found to be highly dependent on the applied potential and on the concentration of the base in the solvent.

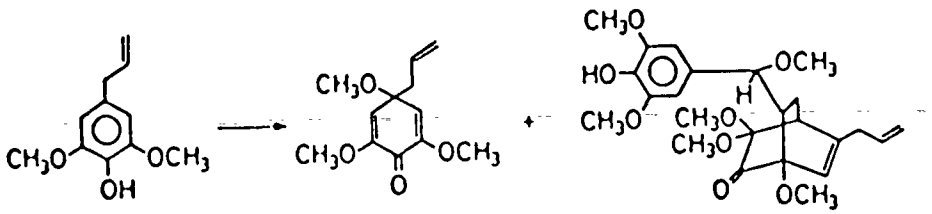


Figure 15. Oxidation of 2,6-dimethyl-4-allylphenol.[59]

Cleavage to form a quinone often depends on the nature of the benzylic substituent and the solvent. Steelink and Britton[63] found that α-methylsyringyl alcohol could be converted into 2,6-dimethoxy-p-benzoquinone in water-acetonitrile

using tetrabutylammonium perchlorate as a supporting electrolyte. In the absence of water, acetosyringone was produced (Fig. 16).

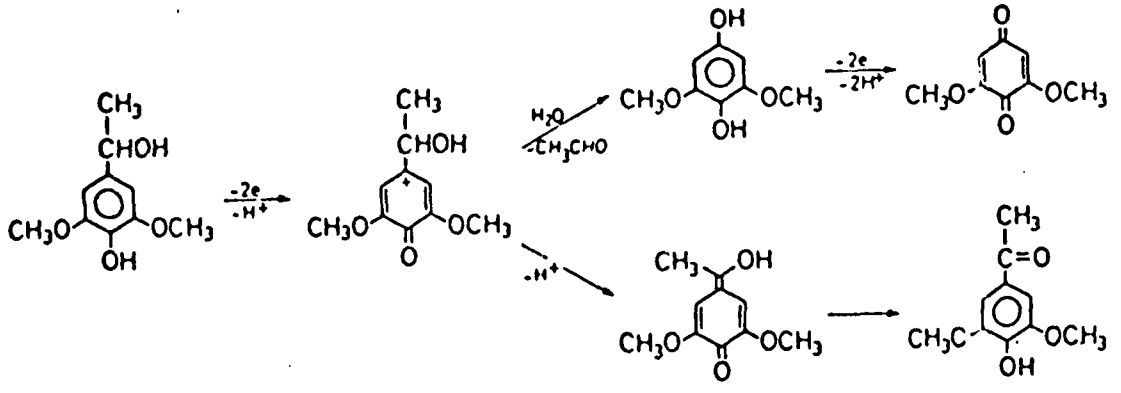


Figure 16. Electrochemical oxidation of a secondary benzyl alcohol.[63]

A mechanism proposed for the conversion to the quinone is presented in Fig. 17. Under similar conditions, oxidation of acetosyringone led to the production of 3,4-dihydroxy-5-methoxyacetophenone.[64] In both cases cyclic voltammetry was found helpful in determining the potential at which the electrolysis was run.

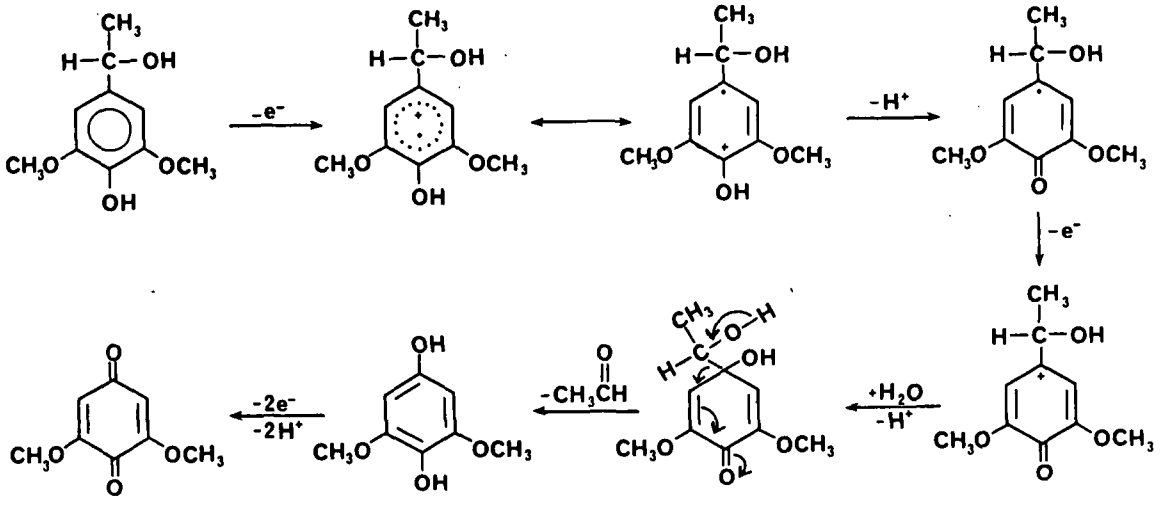


Figure 17. Mechanism for the electrochemical oxidation of α-methylsyringyl alcohol.[63]

Several studies on the electrochemical oxidation of lignin have been made. Cauquis, Limosin, and Pierre[65] found that the products generated in the aqueous alkaline oxidation of kraft and dioxane lignin varied depending on the type of lignin used and on the presence or absence of oxygen in the reaction medium.

Demin, et al.[66] conducted the electrochemical oxidation of lignin isolated from black liquor and unbleached kraft pulp. Infrared analysis indicated a decrease in the phenolic hydroxyl and methoxyl group contents and an increase in carboxyl group contents. Prolonged oxidation caused a degradation of chromophoric groups in the lignin.

Demin, Davydov, and Bogomolov[67] investigated the oxidation of dioxane lignin derived from kraft pulp with and without the addition of potassium dichromate. The addition of 0.025% potassium dichromate to the electrolyte was found to increase the rate of oxidation and degradation.

In a study of the kinetics and mechanism of the anodic oxidation of kraft lignin, Anisimova, et al.[68] found that the oxidation products depended on the applied anode potential. While oxidation was accompanied by polymerization with potentials up to 0.615 V, further increases in potential led to degradation of the lignin and a decrease in molecular weight.

Using various electrodes, Kovalenko, Smirnov, and Shalimov[69] investigated the electrolysis of lignin dissolved in NaOH. There appeared to be a greater degree of phenolic hydroxyl group oxidation on platinum and nickel anodes than on copper or graphite anodes. With electrolysis time up to 25 min, the yields of low-molecular-weight products and carbon dioxide increase rapidly as the phenolic hydroxyl group content decreased. It was theorized that this initial electrolysis stage involved the conversion of benzenoid structures into quinones.

The increase in phenolic hydroxyl group content with prolonged electrolysis time was attributed to demethoxylation and the formation of polyhydric phenols.

In an investigation of the electrochemical oxidation of hydrolysis lignin in alkali, Kovalenko, Shifron, and Raskin[70] found that the rate of oxidation was increased by the introduction of catalysts such as cerium, hypochlorite, and periodate ions.

Lignin degradation and changes in spectral characteristics in the visible and UV range were studied by Stromskii and Chupka[71] during the electrochemical oxidation of lignin in alkali. It was found that current density and the addition of a catalyst/transfer agent played major roles in the reduction of the color of the solution. There appeared to be a linear dependence of the lignin oxidation rate on the transfer agent concentration and an exponential dependence on the current density.

Stromskii and Chupka used potassium ferricyanide as a catalyst/transfer agent in their work. In an alkaline medium, the ferricyanide ion oxidizes lignin and in the process is reduced to the ferrocyanide ion. The ion is easily oxidized back to the ferricyanide ion on a nickel anode. It was noted that other ions of variable-valence metals have also been used effectively as catalyst/transfer agents during the oxidation of organic compounds. For the electrochemical oxidation of lignin, Cl^{+3}, ClO^{-}, and $Cr_2O_7^{-2}$ performed well.

Yoshiyama, et al.[72] recently electrochemically oxidized three hardwood sulfite lignin samples at lead dioxide and platinum anodes under both acidic and alkaline conditions. The lead dioxide anode in sodium hydroxide solution gave the best results; small amounts of about thirty degradation products consisting of aliphatic and aromatic compounds having single substituted benzene nuclei

were detected and analyzed by high-performance liquid chromatography. Product distribution was greatly affected by current density and amount of charge passed.

Like chemical oxidations, electrochemical reactions can sometimes lead to unwanted products. Electrochemical oxidation of lignin units containing benzylic alcohols and ethers, for example, could result in oxidation of the oxygen-containing function in the benzylic position to an aldehyde or a carboxylic acid rather than oxidation of the entire phenolic unit to a quinone.[59] Carboxylic acids can be further converted into other products.[73]

Through the use of cyclic voltammetry, Sundholm[74] found that the first electron transferred from low-molecular-weight compounds related to softwood lignin was followed by very fast reactions leading mainly to polymers. In a study of the oxidation of about twenty dimeric lignin model compounds, Limosin, et al.[75] noted the difficulty in using a platinum electrode due to adsorption phenomenon or the deposition of a nonconducting film. Mainly polymeric products were found; it was concluded that it was not very likely that the electrochemical oxidation of lignin in nonaqueous media would lead to depolymerization of the material.

As in the case of chemical oxidation, electrochemistry results in products which are highly dependent on reaction variables. The use of acidic conditions appears more likely to yield desirable quinone structures from lignin-related compounds. Because of the insolubility of lignin in acid, however, a two-step approach to oxidation may be necessary in which basic conditions are first used to degrade lignin into smaller, more easily solubilized, fragments.

The use of electrochemistry to convert lignin and lignin-related compounds into quinones might be a clean and efficient technique to use in an industrial application. The large number of variables involved in the process, however, could make finding appropriate reaction conditions much more difficult than finding corresponding conditions in a chemical oxidative procedure.

Biochemical Modifications

Several studies of the enzymatic degradation of lignin-related compounds have been conducted.[76-79] The production of methoxy-p-benzoquinone from vanillin and 2,6-dimethoxy-p-benzoquinone from syringic acid has been demonstrated.

Certain Basidiomycetes known as "brown-rot" fungi cause the methoxyl content of lignin to decrease greatly. Kirk and Adler[80] found that the fungus Lenzites trabea Pers. ex Fries causes a net demethylation of the phenolic guaiacyl and syringyl units in sweetgum lignin. This results in the formation of catechol structures.

A certain amount of aromatic hydroxylation, generally ortho to the hydrocarbon side chains, also occurs as a result of the fungal action.[81] Fungi can demethylate both phenolic and etherified units of the guaiacyl and syringyl type within the lignin molecule; the nonphenolic units, however, are not as extensively attacked.[82] Greater demethylation is noted on syringyl units than on guaiacyl units.

More recent work on the biodegradation of lignin has focused on white-rot fungi.[83-85] The action of white-rot fungi on lignin appears to be more severe than that of brown-rot fungi, resulting in much more complete catabolism of the

polymer.[86] While their modes of attack are similar in many respects, brown-rot fungi apparently lack an efficient ring-cleaving system.

Lignin preparations have also been enzymatically degraded to generate p-benzoquinones. Ishihara and Miyazaki[87] isolated 2,6-dimethoxy-p-benzoquinone from enzymatically degraded maple milled-wood lignin. The same quinone was obtained in 1-2% yield from alkali lignin samples by Young and Steelink.[88]

MODIFICATION AND STABILIZATION OF QUINONES

From the discussion above, it is clear that there are several ways in which lignin and lignin-related compounds can be oxidized to generate quinone materials. During pulping, a small portion of lignin is also converted into quinones. These o- and p-benzoquinones, however, are probably not effective catalysts because they are rapidly attacked by pulping reagents and degraded during the rather severe pulping process. As discussed earlier, for a compound to function as a catalyst, it must be relatively stable during pulping, have a suitable solubility in the pulping liquor, and an appropriate balance between its affinity for water and for the lignocellulosic material. Because pulping catalysts act through redox cycles, these compounds must also have reduction potentials which readily permit conversion between reduced and oxidized forms.

Most of the fragmentation reactions of benzoquinones result from attack of a nucleophile at the "nonaromatic" carbon-carbon double bond of the quinone ring. As shown in Fig. 18, this can easily occur in a high temperature alkaline environment. Similar reactions on higher-order quinones, such as anthraquinones and phenanthrenequinones, generally do not take place because they simultaneously involve the loss of aromaticity of an associated benzene ring.[57] It is for this

reason that anthraquinones are generally much more resistant to aqueous base and to oxidation than are benzoquinones and naphthoquinones.

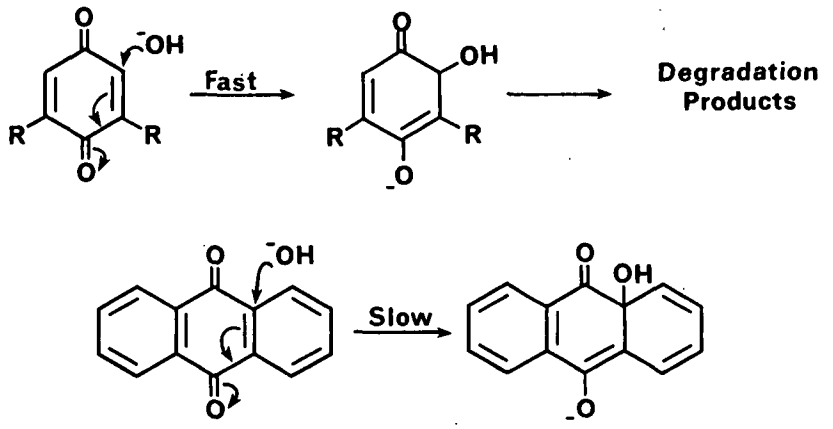


Figure 18. Nucleophilic attack on benzoquinones vs. higher-order quinones.

The Diels-Alder Reaction

Benzoquinones, which are susceptible to alkaline degradation, can be chemically converted to more stable, higher-ring analog quinone or hydroquinone compounds by means of Diels-Alder reactions. The Diels-Alder chemistry of some quinones is well known;[89] for example, one method of generating anthraquinone involves reacting p-benzoquinone with two equivalents of butadiene.[90] As shown in Fig. 19, quinone synthesis using the Diels-Alder reaction involves three steps: the addition of a conjugated diene to a starting quinone, aromatization of the adduct, and oxidation of the resulting quinol to a quinone.[51]

Through the use of a Diels-Alder reaction, simple quinones may be transformed into "condensed" quinones and hydroquinones. With the appropriate selection of a diene, it is possible to convert unstable benzoquinone structures of low pulping catalytic activity into more stable, more active naphthoquinone, anthraquinone, or phenanthrenequinone structures. Because the first step in catalytic delignification involves conversion of the catalyst to its reduced

form, the final oxidation step in the sequence shown in Fig. 19 may not be necessary.

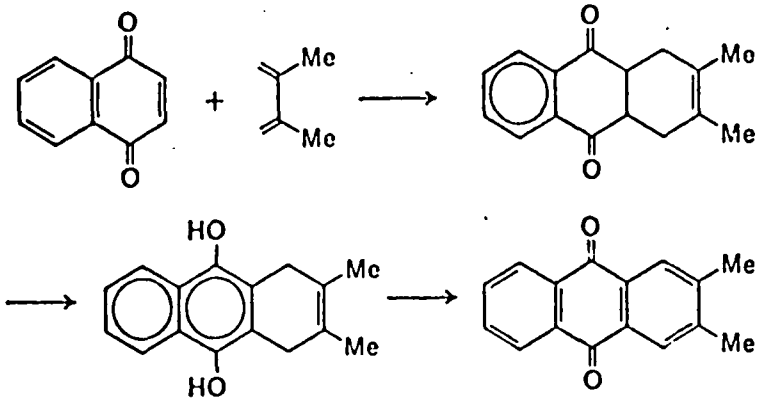


Figure 19. Quinone synthesis using the Diels-Alder reaction.[51]

The fusion of a benzene ring onto an existing quinone is most easily accomplished on a ring which has two adjacent positions unsubstituted.[51] Addition may still take place if substituents are present, however, and yields are usually good. For large-scale reactions, it may be advantageous to add a polymerization inhibitor. Diels-Alder reactions may be catalyzed with various compounds, including metallic chlorides and zeolites.[91-93]

Aromatization and oxidation can be achieved in several ways. Aeration in alkaline solution, for example, can be used for anthraquinones. Aromatization of a dihydronaphthoquinone to a naphthoquinone occurs rapidly on warming with hydrochloric acid containing stannous chloride.[94] Oxidation can then be achieved with acid dichromate. It is also possible to first oxidize with nitrous acid and then dehydrogenate with chromic acid. Adducts formed from halogenated quinones readily aromatize by loss of hydrogen halide.

Substituents can control the direction of the Diels-Alder reaction.[95-97] The addition occurs preferentially at the more electron-deficient double bond. Steric factors, however, are also important, and the number and size of potential angular substituents as well as substituents on the diene can influence the course of the reaction.

Although the Diels-Alder reaction has great potential for extending the ring structure of quinones, there are other possibilities. Reactions with α,β-unsaturated aldehydes[98] and cyclic anhydrides,[51] for example, have been used to convert benzoquinones into both naphthoquinones and anthraquinones.

Modification of p-Quinones

Most of the work done using the Diels-Alder reaction involves p-quinones. Fieser,[94] for example, developed a useful technique for the synthesis of p-naphthoquinones from p-benzoquinones and showed that the use of acetic acid as a solvent avoids the need to work up the intermediate adduct. Hiranuma and Miller have used both 1,4-dimethoxy-1,3-butadiene[99] and 1,4-di-tert-butoxy-1,3-butadiene[100] in reactions with p-quinones. Reaction of 1,4-dimethoxy-1,3-butadiene with p-benzoquinone and p-naphthoquinone yielded adducts that lost one and two molecules of methanol, respectively.

Shimo, Somekawa, and Kumamoto[101] found that 2-pyrones combined with p-benzoquinones in Diels-Alder reactions. In addition to the Diels-Alder adducts, p-naphthoquinones and anthraquinones were produced. Cava, Deana, and Muth[102] synthesized 1,4-anthraquinone from p-benzoquinone by using a phenyl tetrabromide compound. Torssell[103] found that thiophene and substituted thiophenes could also be used in Diels-Alder reactions with p-benzoquinone to produce juglone and p-naphthoquinones.

Although electron-donating groups would be expected to deactivate quinones toward Diels-Alder syntheses, reactions of these compounds have been reported, including those of several methoxy quinones. Birnbaum,[104] for example, found that a mixture of methoxy-p-benzoquinone and butadiene gave an 85% yield of the Diels-Alder adduct, 2-methoxy-4a,5,8,8a-tetrahydronaphthoquinone.

Tegmo-Larsson, Rozeboom, and Houk[96] found both 2,5-dimethyl-p-benzoquinone and 2,6-dimethoxy-p-benzoquinone reacted with several dienes to produce good yields of the Diels-Alder adducts. Methanol was readily eliminated from the dimethoxy adducts, and the resulting dihydroxynaphthoquinones were easily air oxidized to the naphthoquinones. Similarly, both 2-methyl- and 2-methoxy-p-naphthoquinones formed Diels-Alder adducts with the same dienes.

Fieser and Seligman[105] found that 2,6-dimethyl-p-naphthoquinone readily reacted with 2,3-dimethyl-1,3-butadiene to give an addition product in nearly quantitative yield. Dehydrogenation with sulfur produced 2,3,6-trimethyl-anthraquinone in good yield. The bridge methyl group apparently was eliminated as methane.

Methoxy-p-benzoquinone combines with both styrene and o-methylstyrene to form the corresponding phenanthrenequinones.[106] The Diels-Alder reactions of 2,6-dimethoxy-p-benzoquinone with several dienes have been found to be catalyzed by $TiCl_4$.[91]

The compound 1,4-naphthoquinone has been found to combine with myrcene, and the Diels-Alder adduct has been oxidized with a cupric salt and with air in the presence of both weak and strong bases.[107] The ring structure of the adduct has been further enhanced through reaction with acetic acid.[108] Use of the

resultant quinones in pulping has been found to increase both the rate and the yield of the reaction.

Modification of o-Quinones

The Diels-Alder chemistry of several o-quinones has also been studied. Ansell and Murray[109] showed that o-naphthoquinone reacts readily with 2,3-dimethyl-1,3-butadiene in boiling chloroform solution to give 2,3-dimethyl-9,10-phenanthrenequinone. As shown in Fig. 20, the reaction proceeds by way of the Diels-Alder adduct which then enolizes and readily dehydrogenates to produce the phenanthrene-9,10-diol. Air oxidation yields the phenanthrenequinone.

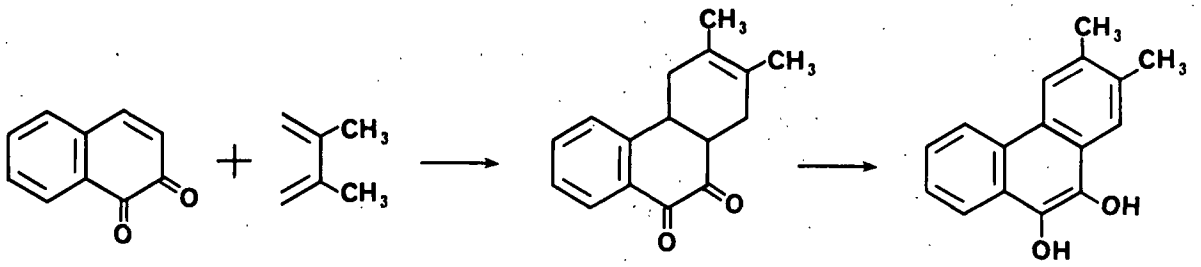


Figure 20. Diels-Alder reaction of o-naphthoquinone.[109]

Ansell and Murray[109,110] found that several o-naphthoquinones with electron withdrawing groups in the 3- or 4-position also underwent addition to the 3,4-double bond. The reaction of 3,7-dimethyl-1,2-naphthoquinone with 2,3-dimethyl-1,3-butadiene was observed by Fieser and Seligman.[105]

Even though o-benzoquinones are more sensitive than o-naphthoquinones, several successful Diels-Alder reactions are known. It has been observed that o-benzoquinones can behave as either dienophiles or as dienes.[51] In several solvents 3-methoxy-1,2-benzoquinone, for example, reacts with itself to form the adduct shown on the left in Fig. 21. Upon oxidation with periodate, however, the adduct gives the quinone on the right in high yield.[29,30]

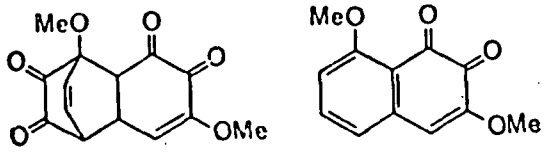


Figure 21. Diels-Alder addition product of 3-methoxy-1,2-benzoquinone.[29]

Realizing that the lack of reactivity of o-benzoquinones toward acyclic dienes was probably due to the fact that the rate of o-benzoquinone decomposition and dimerization was much faster than the rate of its Diels-Alder reaction, Ansell, et al.[111] demonstrated that many o-benzoquinones would react if large excesses of dienes were used. The adducts readily underwent aromatization to give the corresponding naphthalene derivatives. Table 1 indicates the large number of o-benzoquinones that were successfully reacted with 2,3-dimethylbutadiene.

Table 1. Reaction of 2,3-dimethylbutadiene with o-benzoquinones.[111]

Quinone Substituent	Yield of Adduct (%)	Site of Addition
H	51	3,4 = 5,6
3-Me	27	5,6
4-Me	39	5,6
3-MeO	75	5,6
4-MeO	80	5,6
3-Cl	ca. 90	5,6
4-Cl	60	5,6
4-NHAc	87	5,6
4-COOMe	75	3,4
4-CN	19	3,4
3-Me, 4-Me	61	5,6
3-Me, 5-Me	44	3,4 and 5,6
3-Me, 6-Me	63	3,4 = 5,6
4-Me, 5-Me	54	3,4 = 5,6
3-Me, 5-COOMe	34	5,6
4-Me, 5-COOMe	63	5,6
4-MeO, 5-COOMe	57	5,6
3-Me, 5-CN	13	5,6
3-Cl, 4-Cl, 5-Cl	17.5	5,6
3-Cl, 4-Cl, 6-Cl	72	5,6
3-Me, 4-Me, 6-Me	26	5,6

EXPERIMENTAL APPROACH

As stated earlier, the objectives of this thesis are the generation of quinones from lignin and lignin-related compounds, the enhancement of the ring structures of these quinones through the use of Diels-Alder reactions, and the testing of the compounds generated for activity as pulping catalysts. The eventual goal of the work is to produce a useful pulping catalyst from lignin.

The approach taken to satisfy these objectives can be divided into three parts. Initial experimental work was aimed at determining the extent to which lignin can be converted into a pulping catalyst through simple oxidation procedures alone. A short time was spent using chemical and electrochemical techniques to oxidize lignin samples; these samples were then tested for catalytic activity. Evaluation of the oxidized samples was by the degree to which they were effective in degrading a lignin model compound and through actual pulping on a laboratory scale.

The second part of the experimental work was a detailed investigation of the generation and testing of Diels-Alder adducts of lignin model quinones. The p-benzoquinones used, methoxy- and 2,6-dimethoxy-p-benzoquinone, can actually be obtained from lignin through cleavage of the propyl side chain from free-phenolic lignin units. Three 4-substituted o-benzoquinones, models for lignin units which have undergone oxidation to quinones without side-chain loss, were also investigated.

Three dienes were selected for use in the Diels-Alder reactions: 2,3-dimethyl-1,3-butadiene, isoprene, and styrene. Throughout the experimental work, possible practical application to an industrial process was kept in mind.

Although less reactive as dienes than dimethylbutadiene, isoprene and styrene are cheap and readily available compounds.

After completion of the second part of the experimental work, it became clear that the best chance for success in producing a pulping catalyst from lignin was through Diels-Alder modification of p-benzoquinone starting compounds. The third part of the experimental work was therefore aimed at finding oxidative procedures for successfully generating methoxy- and 2,6-dimethoxy-p-benzoquinone from various lignin and lignin-related samples. Both chemical and electrochemical investigations were undertaken. Based on the literature survey, it was felt that thermal/chemical techniques would generally result in the production of undesirable o-quinones and that enzymatic techniques were beyond the scope of the thesis.

An outline of the path followed in the experimental work is presented in Fig. 22.

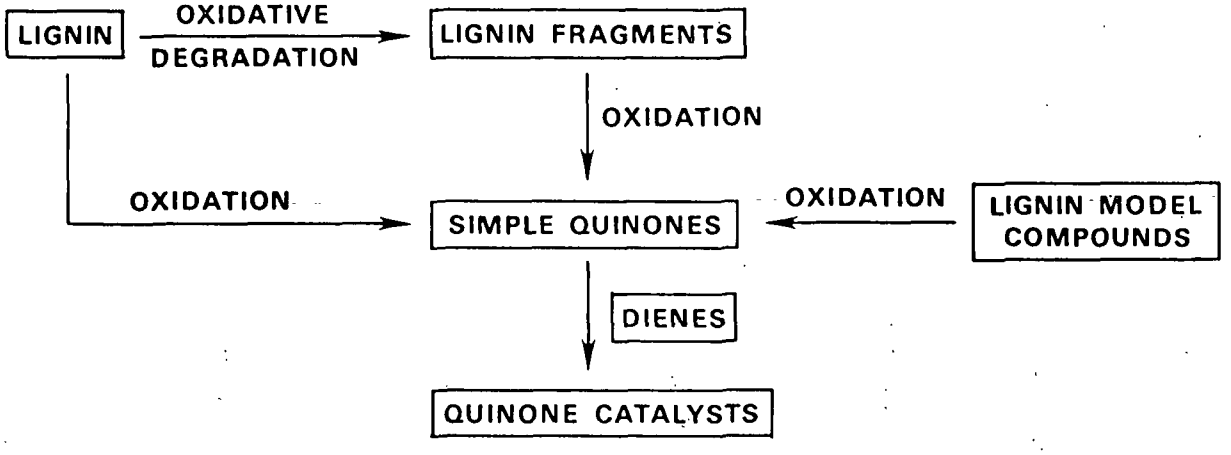


Figure 22. Outline of the experimental work.

EXPERIMENTAL PROCEDURES

DIRECT OXIDATION OF LIGNIN

Soda Lignin Isolation

Lignin was isolated from the black liquor resulting from a soda cook of loblolly pine chips. The cooking conditions are presented in Table 2. The unscreened pulp yield was 53.4%; the kappa number was determined by TAPPI Method T 236 to be 96.0.

Table 2. Cooking conditions of loblolly pine chips.

NaOH (as Na_2O, % on wood)	18
Liquor ratio (cm^3/g)	4
Cooking schedule:	
Time at 90°C (min)	15
Time from 90° to 173°C (min)	90
Time at 173°C	94
H-factor	2100

The lignin was precipitated from the black liquor by acidification to a pH between 2 and 3 through the dropwise addition of 6M H_2SO_4. The precipitated lignin was then centrifuged and repeatedly washed with distilled water until the pH of the supernatant was between 5 and 6. The isolated lignin was freeze dried and stored in an amber glass bottle under nitrogen.

Carbohydrate removal was achieved by dissolving the lignin in 2-methoxyethanol followed by successive filtration through coarse and medium sintered-glass Buchner funnels. The solvent was then removed on a rotary evaporator at 40-45°C, and the resulting syrup was dried in a vacuum desiccator over P_2O_5. The dry lignin residue was flushed from the flask with distilled water, freeze

dried, and stored in an amber glass bottle under nitrogen; this sample was designated as U1.

A second purification scheme was applied to some of the lignin which was subsequently oxidized electrochemically. This lignin was first dissolved in 0.2N NaOH and then precipitated using 6M H_2SO_4. After the resulting mixture was centrifuged to compact the lignin, the supernatant was decanted, and the lignin was washed three times with distilled water. The isolated lignin was dried in a vacuum oven at 45°C and also stored as just described; this sample was designated as U2.

Electrochemical Oxidation

Apparatus

The electrochemical oxidation of the lignin samples was performed at the Solar Energy Research Institute, Golden, CO. A schematic drawing of the equipment setup that was used is presented in Fig. 23.

The electrochemical cell consisted of a hand-blown glass anode compartment of approximately 400 mL total capacity and a smaller cathode chamber constructed from a Teflon cylinder. The cell was designed so that the cathode chamber fit inside of the anode compartment. A Dupont Nafion No. 125 perfluorinated membrane was placed at the bottom of the cathode chamber to separate the two halves of the cell.

The working electrode was constructed from a 5-cm diameter metal disk which was soldered to a copper wire. The connecting wire was surrounded by a glass tube which was attached to the metal disk with epoxy resin; both the wire and the soldered joint were completely covered by the glass tube and/or resin. The

counter electrode consisted of a platinum wire coil. A Beckman saturated calomel reference electrode was used.

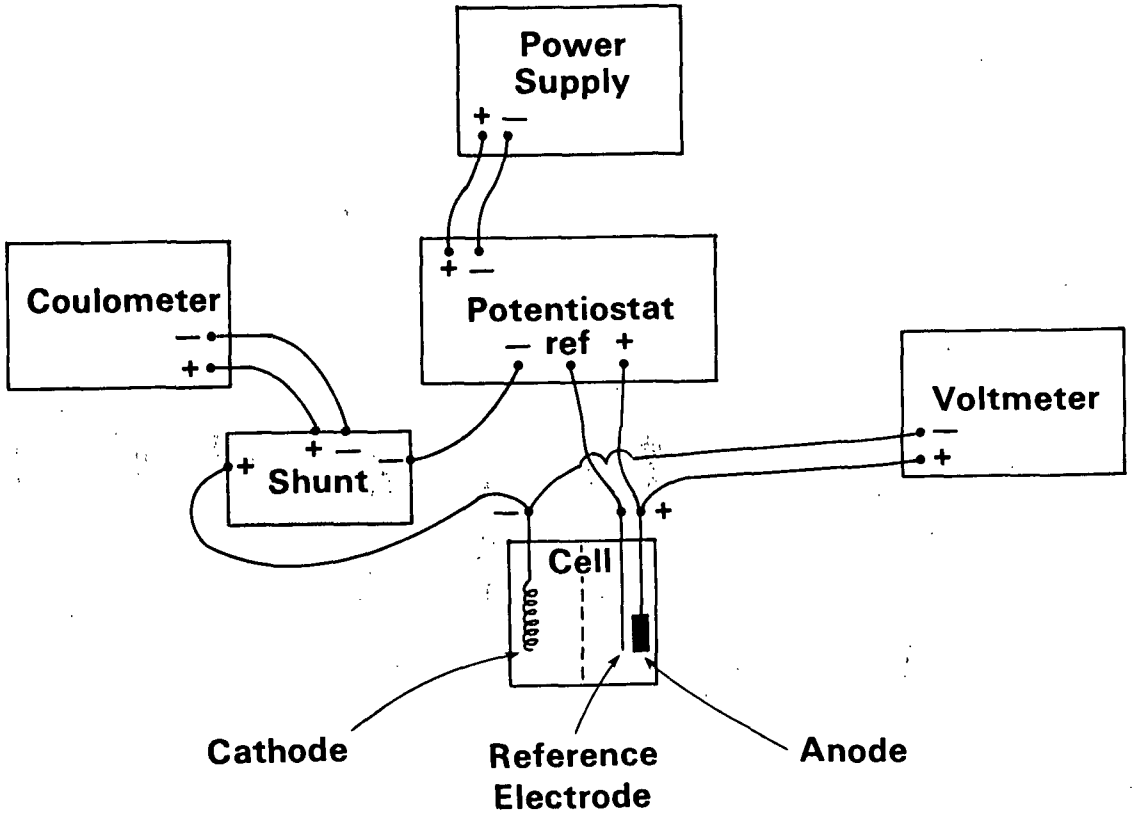


Figure 23. Equipment setup for electrochemical oxidations.

The cell was connected in series with an EG & G Princeton Applied Research Model 371 Potentiostat-Galvanostat and an Electrosynthesis Model 640 coulometer equipped with a Model 645 shunt. A digital voltmeter was used to measure the cell potential.

Soda Lignin Electrochemical Oxidation

Prior to any of the reactions, the Nafion membrane was pretreated by boiling it in the electrolyte to be used for 1 hour and then stored in the electrolyte. Working electrodes and the counter electrode were cleaned in

dilute nitric acid and thoroughly rinsed with distilled water. If necessary, 180-grit carbide grinding paper was used to polish the working electrodes by removing any deposits that had formed during the previous experiment. The coulometer was periodically checked for proper calibration by connecting it in series with known resistances and passing a known current through the circuit for a measured amount of time.

After filling the cell with the electrolyte to be used (NaOH, 0.20 to 1.00N, 150 to 200 mL anolyte), inert gas was bubbled through the solution to remove most of the dissolved oxygen. The anode was then pretreated at 0.800 V for approximately 10 minutes to generate an oxidized, reproducible surface. The lignin was then added (0.020 g/mL), and the electrolysis was carried out. Although background polarization curves (current vs. potential) were obtained before and after the addition of the lignin to help determine an appropriate potential at which to run the reaction, electrolyses were generally conducted between 0.750 and 0.800 V. The amount of charge passed through the lignin solution was varied up to 6000 coulombs/g.

Upon completion of the electrolysis, the anolyte was removed from the cell and acidified with 6M H_2SO_4 until the lignin precipitated (pH approximately 3). The lignin was obtained by centrifuging the anolyte and decanting the supernatant; the lignin was then washed twice with distilled water, again using centrifugation to compact the fine particles. The isolated lignin was dried in a vacuum oven at 45°C.

For several samples an acid-soluble lignin fraction was also isolated. This fraction was obtained from the supernatant by saturating it with KCl, filtering out the undissolved salt, and extracting with ethyl acetate (3 x 100

mL). The extract was then washed with 100 mL saturated NaCl and dried over anhydrous $MgSO_4$. The solvent was removed on a rotary evaporator at approximately 30°C; final traces of solvent were removed under high vacuum.

Infrared (IR) spectra were obtained of both oxidized and unoxidized lignin samples by pressing the lignin into KBr pellets containing 0.114% KSCN as an internal standard.[112] Pellets were made using a mixture of 0.6 mg lignin and 120.0 mg KSCN/KBr. Spectra of the acid-soluble lignin samples were obtained using NaCl disks by dissolving the lignin in acetone, applying a few drops of the solution to the disk, and then evaporating the solvent under a stream of nitrogen. A Perkin Elmer 599B IR Spectrophotometer was used.

Because of the difficulty in weighing an exact amount of such a small quantity of lignin, it was decided not to base the IR analysis on the KSCN internal standard. Instead, the analysis was carried out by comparing the absorbance due to carbonyl stretching at 1715 cm^{-1} to that due to aromatic skeletal vibration at 1510 cm^{-1}.[113] This would give some indication of the extent of oxidation by indicating the degree to which the original lignin phenyl-propane units were converted into carbonyl structures.

Oxidation of Soda Lignin with Potassium Thiophenoxide

Soda lignin, which had been purified through carbohydrate removal as described above, was oxidized according to the method of Francis and Reeve[114,115] as described below.

Freshly distilled tetrahydrofuran (THF, 200 mL) was added to a 500-mL, 3-neck, round-bottom flask equipped with a stirring bar. A gentle flow of nitrogen was admitted through one of the necks; the other two necks were stoppered. Potassium (1.7 g) was cut into small pea-size pieces and added to the

THF. Thiophenol (5.00 mL) was then added and the reaction was allowed to proceed with stirring for 1 hour. After reaction, unreacted potassium was scooped out, and the THF was evaporated through gentle heating.

Lignin (1.00 g) was added along with 150 mL of 2-hydroxyethyl ether to the reaction flask containing the potassium thiophenoxide. A thermometer was inserted into one of the necks of the flask, and the temperature was raised to 200°C and maintained there for 30 minutes. After the flask was cooled to room temperature, 200 mL of H_2SO_3 (prepared by bubbling SO_2 through water until saturated) was added and allowed to react for 10 minutes. The precipitated lignin was isolated by centrifugation, washed once with 100 mL H_2SO_3 and three times with water, and freeze dried.

The degree of oxidation was ascertained by determining change in weight and change in methoxyl content; the results of these analyses are presented in Table 3. Methoxyl analyses were performed by Chem-Lig International, Inc., Schofield, WI, using the Zeisel method; although duplicate analyses are routinely done, four determinations were made for the sample obtained before oxidation because of the large degree of variability encountered.

Table 3. Analysis of lignin oxidized by potassium thiophenoxide.

Weight		Methoxyl Content	
Before Oxidation (g)	After Oxidation (g)	Before Oxidation (wt.%)	After Oxidation (wt.%)
1.00	1.13	13.60	2.81
		8.28	2.86
		18.14	
		14.47	

Evaluation of Catalytic Activity

Oxidized soda lignin samples were tested for possible delignification catalytic activity through laboratory pulping and determination of yield and kappa number. Soda pulping of southern pine was performed using stainless-steel pressure vessels with a maximum capacity of 70 g oven-dry wood. The same conditions as presented in Table 2 were used with an additive level of 1%.

GENERATION AND TESTING OF DIELS-ALDER ADDUCTS OF LIGNIN MODEL QUINONES

The following section includes the procedures that were followed in the syntheses of both lignin model quinones and Diels-Alder adducts of these quinones. Where applicable, procedures are followed with results of analytical work done to verify the structures of compounds synthesized. Melting points were obtained using a Thomas Hoover Capillary Melting Point Apparatus and are uncorrected. NMR spectra were recorded on a Jeol FX 100 spectrometer using TMS as an internal reference. Parentheses following the signals indicate the splitting patterns (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad signal), integration areas, and signal assignments. Infrared (IR) spectra were recorded on a Perkin-Elmer Model 700 Infrared Spectrometer and standardized with polystyrene.

Gas chromatographic (GC) analyses were either done on a Hewlett-Packard 5890A GC or combined with mass spectrometric (MS) analyses and performed on a Hewlett-Packard 5985B GC/MS system. The GC/MS system employed helium (30 mL/min) as the carrier gas, a jet separator at 275°, a source temperature of 200° and an ionization voltage of 70 eV. On both instruments a 6-ft, 1/4-inch glass column packed with 3% silicone OV-17 on 100/120 Chromosorb W-HP was used.

Synthesis of Lignin Model Quinones

The lignin model quinones selected for investigation are presented in Fig. 24. As briefly mentioned earlier, the p-benzoquinones could be obtained from lignin through cleavage of the phenyl propane side chain. Methoxy-p-benzoquinone would be obtained from both hardwood and softwood lignins, while the dimethoxy compound, in general, would be obtained only from a hardwood sample.

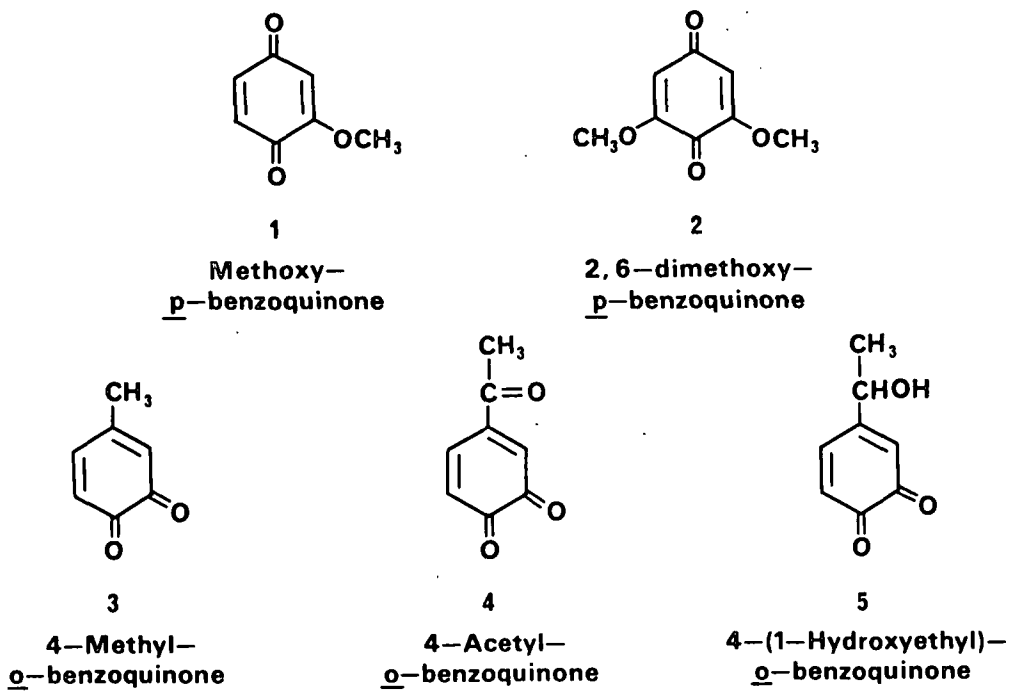


Figure 24. Lignin model quinones.

Oxidation of a phenolic hydroxyl group together with an adjacent methoxyl group in a lignin macromolecule would lead to generation of an o-benzoquinone. This quinone, of course, would remain attached in the lignin matrix via the propyl side chain. The o-quinones presented in Fig. 24 therefore only model this type of quinone in lignin. The three quinones selected for investigation have side chains which represent common features of the side chains actually found in lignin: an α-hydroxyl group, an α-carbonyl group, and a fully saturated carbon atom in the α-position.

Methoxy-p-Benzoquinone,[116] 1

Methoxyhydroquinone[117] (8.15 g) was dissolved in 175 mL of hot, dry benzene in a 500-mL, round-bottom flask equipped with a stirring bar and a reflux condenser. Anhydrous $MgSO_4$ (17.46 g) and PbO_2 (58.19 g) were added and the mixture heated until a sample of the solution deposited yellow crystals upon evaporation (approximately 5 hours). The mixture was then filtered and rinsed with boiling benzene. The filtrate was evaporated, and the crude product was recrystallized twice from n-amyl alcohol and washed with a little cold methanol to give 5.30 g (66%) of 1: m.p. 143.0-144.5°C [lit.[116, 118], m.p. 143-144°, 144-145°]; ^{1}H-NMR (DMSO-d_6) δ 3.78 (s, 3, OCH_3), 6.10 (d, 1, J = 2 Hz, 3-H), 6.75, 6.77 (s, 2, 5- and 6-H).

2,6-Dimethoxy-p-Benzoquinone,[119] 2

A solution of 1.68 g 1,3,5-trimethoxybenzene[120] in 12.6 mL of acetone was added to a solution of 0.20 g $K_3Fe(CN)_6$ in 1.00 mL of water in a 125-mL Erlenmeyer flask equipped with a stirring bar. Hydrogen peroxide (30%, 3.40 mL) was then added, and the mixture was stirred in the dark at room temperature for 15 hours. After reaction, the mixture was diluted with 250 mL of CH_2Cl_2, washed with water (4 x 50 mL), and dried over anhydrous Na_2SO_4. The CH_2Cl_2 was evaporated until crystals first appeared; methanol was then used to precipitate the remaining product to give 1.11 g (66%) of 2: m.p. 253.0-254.0°C; ^{1}H-NMR ($CDCl_3$) δ 3.82 (s, 3, 2- and 6-OCH_3), 5.85 (s, 1, 3- and 5-H).

4-Methyl-o-Benzoquinone, 3

4-Methylcatechol (0.50 g) and a small amount of anhydrous Na_2SO_4 were added to 27 mL of anhydrous ether in a 125-mL Erlenmeyer flask. Under a nitrogen atmosphere in a glove bag, 1.04 g of AgO was added.[35] After being stirred for 7 minutes, the mixture was filtered into 27 mL of cold, dry petroleum ether (b.p.

35-60°C) in a 100-mL, round-bottom flask. A septum was placed over the mouth of the flask; the flask was then removed from the glove bag and immersed into an ethylene glycol bath. The bath temperature was lowered to -25°C by using a dry ice/acetone mixture. Small brownish-red crystals gradually formed; the solvent was removed with a syringe, and the crystals were washed twice with 5-mL portions of cold, dry petroleum ether. Final traces of solvent were removed *in vacuo* to give 0.069 g (14%) of 3: m.p. 74.5-75.5°C [lit.[35], m.p. 74-76°]; ^{1}H-NMR ($CDCl_3$) δ 2.18 (d, 3, J = 1 Hz, 4-CH_3), 6.24 (m, 1, 3-H), 6.34 (d, 1, J = 10 Hz, 6-H), 6.91 (d of d, 1, J = 2, 10 Hz, 5-H).

To synthesize larger quantities of this compound, another procedure was used.[121] A solution of 4.00 g *o*-chloranil in 50 mL of anhydrous ether was added to a solution of 1.90 g 4-methylcatechol[120] in 10 mL of anhydrous ether. The mixture was cooled to -25°C using an ethylene glycol bath in a dry ice/acetone mixture and maintained at that temperature for 5 minutes. The red crystals which formed were filtered and rinsed with two 30-mL portions of anhydrous ether at -25°C to give 1.20 g of 3 (64%): m.p. 72.5-74.5°C.

4-Acetyl-*o*-Benzoquinone,[122] 4

Sodium periodate (1.80 g) dissolved in 20 mL of distilled water was added to 1.40 g of acetovanillone[120] dissolved in 20 mL of glacial acetic acid with constant stirring. After reaction, 1 mL of ethylene glycol was added to consume any unreacted sodium periodate. Because of its high reactivity, the 4-acetyl-*o*-benzoquinone was not isolated.

An appropriate reaction time for the generation of this compound was determined through a gas chromatographic study. After combining the acetovanillone and sodium periodate solutions, 1-mL samples were pulled at various time

intervals, and the reaction was stopped by the addition of 1 mL ethylene glycol. A solution of 4-isopropylphenol (1 mL) prepared by dissolving 0.2867 g of 4-isopropylphenol in 1N NaOH in a 10-mL volumetric flask (mole ratio of 4-isopropylphenol to initial acetovanillone was 1 to 1) was then added. This was followed by the addition of 1 mL saturated sodium bicarbonate solution, to neutralize some of the acetic acid, and extraction with 2 mL of $CHCl_3$. The $CHCl_3$ extracts were analyzed for their acetovanillone and 4-isopropylphenol contents. An OV-17 column was used with a temperature program of 150 to 285°C at 10°/minute. This analysis indicated that a reaction time of approximately 80 minutes was needed for complete reaction of the acetovanillone.

4-(1-Hydroxyethyl)-o-Benzoquinone, 5

Sodium periodate (0.64 g) dissolved in 7 mL of distilled water was added to 0.50 g of α-methylvanillyl alcohol[120] dissolved in 7 mL of glacial acetic acid, with constant stirring. After reaction, 1 mL of ethylene glycol was added to consume any unreacted sodium periodate. Like the previous compound, 4-(1-hydroxyethyl)-o-benzoquinone was not isolated.

An appropriate reaction time was determined through a GC study similar to that described above for 4-acetyl-o-benzoquinone. After combining the reactant solutions, 1-mL samples were pulled at various time intervals, and the reaction was stopped by the addition of 1 mL ethylene glycol. A solution of 4-isopropylphenol (1 mL) prepared by dissolving 0.2891 g of 4-isopropylphenol in 1N NaOH in a 10-mL volumetric flask (mole ratio of 4-isopropylphenol to initial α-methylvanillyl alcohol was 1 to 1) was then added. Neutralization, extraction, and GC analysis were identical to those described above. Analysis indicated that after only one minute the α-methylvanillyl alcohol had been completely consumed by the sodium periodate.

Synthesis of Diels-Alder Adducts

Three criteria were used in the selection of the dienes for use in the Diels-Alder reactions with the lignin model quinones: reactivity, ease of product characterization, and expense on an industrial scale. The three dienes selected are presented in Fig. 25. 2,3-Dimethyl-1,3-butadiene was selected because of its high reactivity and because its symmetry would probably lead to products which could be more easily characterized. Although less active than dimethylbutadiene, 2-methyl-1,3-butadiene (isoprene) is still fairly reactive and is a relatively cheap raw material from the economic point of view. Styrene is not very reactive as a diene; it is, however, even less expensive than isoprene.

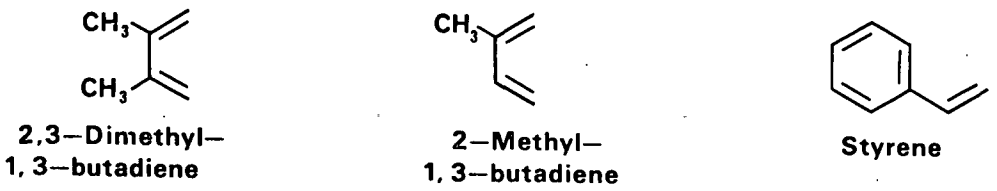
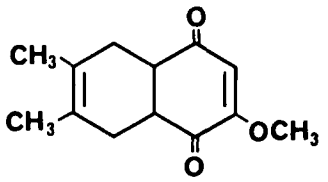


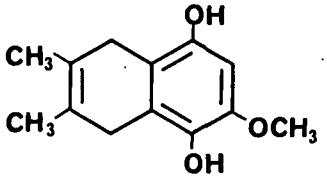
Figure 25. Dienes used in the Diels-Alder reactions.

The Diels-Alder adducts which were synthesized are illustrated in Fig. 26; the experimental procedures used are described below. In several of the reactions in which an elevated temperature was needed, 4.5-mL stainless-steel pressure vessels (minibombs) were used. The bombs were preheated in a water bath at 60°C for 30 minutes before being placed in an oil bath. This was done to better seat the Teflon rings used to seal the bombs and thus prevent the bombs from leaking. In the oil bath the bombs were slowly rotated by means of a chain-drive mechanism; the temperatures and times given below refer to the reaction in the oil bath only.



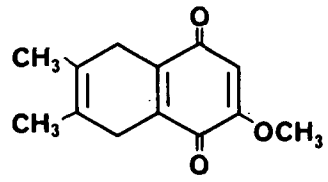
6

4a,5,8,8a-Tetrahydro-2-methoxy-6,7-dimethyl-1,4-naphthoquinone



7

5,8-Dihydro-2-methoxy-6,7-dimethyl-1,4-naphthoquinol



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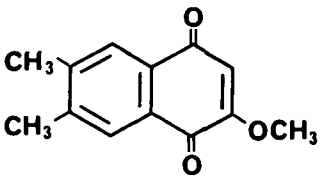
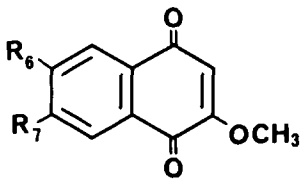
5,8-Dihydro-2-methoxy-6,7-dimethyl-1,4-naphthoquinone



9

2-Methoxy-6,7-dimethyl-1,4-naphthoquinone

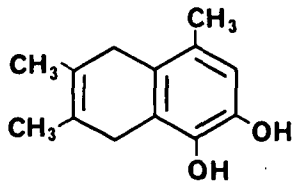


10

2-Methoxy-6- and 7-methyl-1,4-naphthoquinone

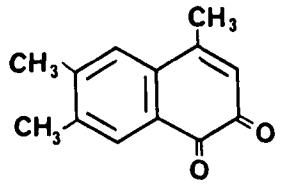
10a, $R_6 = CH_3$, $R_7 = H$

10b, $R_7 = CH_3$, $R_6 = H$



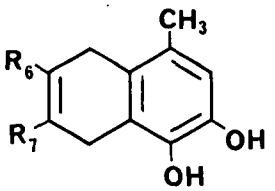
11

5,8-Dihydro-4,6,7-trimethyl-naphthalene-1,2-diol



12

4,6,7-Trimethyl-1,2-naphthoquinone



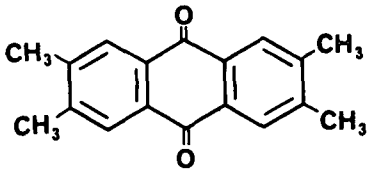
13

5,8-Dihydro-4,6- and 4,7-dimethyl-naphthalene-1,2-diol

13a, $R_6 = CH_3$, $R_7 = H$

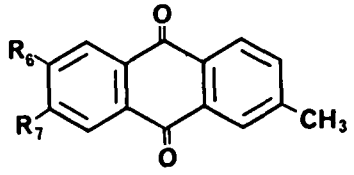
13b, $R_7 = CH_3$, $R_6 = H$

Figure 26. Diels-Alder adducts of lignin model quinones (continued).



14

2,3,6,7-Tetramethylanthraquinone

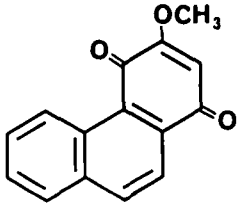


15

2,6- and 2,7-Dimethylanthraquinone

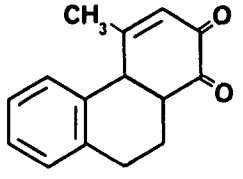
15a, $R_6 = CH_3$, $R_7 = H$

15b, $R_7 = CH_3$, $R_6 = H$



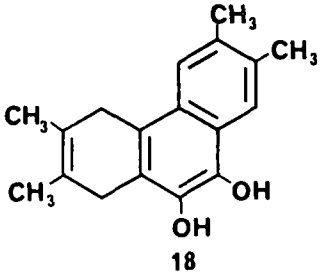
16

3-Methoxyphenanthrene-1,4-quinone



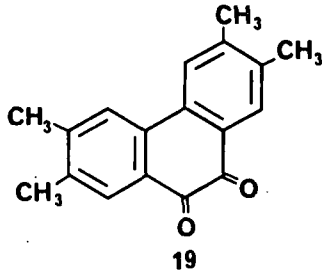
17

4a,9,10,10a-Tetrahydro-4-methyl-phenanthrene-1,2-quinone



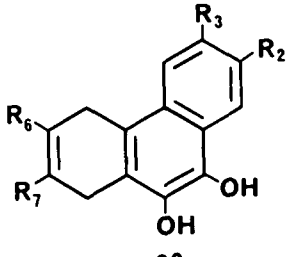
18

1,4-Dihydro-2,3,6,7-tetramethyl-phenanthrene-9,10-diol



19

2,3,6,7-Tetramethyl-phenanthrene-9,10-quinone



20

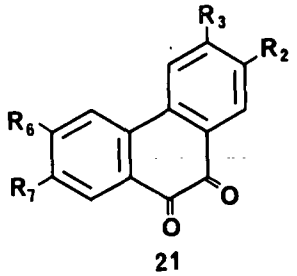
1,4-Dihydro-2,6-, 2,7-, 3,6-, and 3,7-dimethylphenanthrene-9,10-diol

20a, $R_2 = R_6 = CH_3$, $R_3 = R_7 = H$

20b, $R_2 = R_7 = CH_3$, $R_3 = R_6 = H$

20c, $R_3 = R_6 = CH_3$, $R_2 = R_7 = H$

20d, $R_3 = R_7 = CH_3$, $R_2 = R_6 = H$



21

2,6-, 2,7-, and 3,6-Dimethyl-phenanthrene-9,10-quinone

21a, $R_2 = R_6 = CH_3$, $R_3 = R_7 = H$

21b, $R_2 = R_7 = CH_3$, $R_3 = R_6 = H$

21c, $R_3 = R_6 = CH_3$, $R_2 = R_7 = H$

Figure 26. Diels-Alder adducts of lignin model quinones (concluded).

4a,5,8,8a-Tetrahydro-2-Methoxy-6,7-Dimethyl-1,4-Naphthoquinone,[95] 6

Methoxy-p-benzoquinone (0.50 g) and 2,3-dimethyl-1,3-butadiene (0.62 mL) were added to 23 mL of methanol in a 100-mL, 3-neck, round-bottom flask equipped with a stirring bar, thermometer, and reflux condenser. The solution was heated at 45°C for 18.5 hours and then reduced in volume to approximately 2 mL. With cooling, crystallization occurred. Recrystallization several times from petroleum ether (b.p. 50-110°C) produced 0.19 g (24%) of 6: m.p. 133.5-134.5°C [lit.[95], m.p. 140.0-141.5°]; ^{1}H-NMR ($CDCl_3$) δ 1.62 (s, 6, 6- and 7-CH_3), 2.0-2.5 (br, 4, 5- and 8-H_2), 3.0-3.3 (br, 2, 4a- and 8a-H), 3.78 (s, 3, OCH_3), 5.87 (s, 1, 3-H).

5,8-Dihydro-2-Methoxy-6,7-Dimethyl-1,4-Naphthoquinol,[95] 7

Compound 6 (0.50 g) was dissolved in approximately 2 mL of boiling glacial acetic acid. When 2 drops of concentrated HCl was added, a white precipitate immediately formed. This was recrystallized from 95% ethanol to give 0.39 g (79%) of 7: m.p. 212-214°C [lit.[95], m.p. 209-211°]; ^{1}H-NMR (acetone-d_6) δ 1.75 (s, 6, 6- and 7-CH_3), 3.15 (s, 4, 5- and 8-H_2), 3.74 (s, 3, 2-OCH_3), 6.40 (s, 1, 3-H), 6.51, 7.31 (s, 2, 1- and 4-OH).

Compound 7 was also obtained by the reaction of 0.20 g methoxy-p-benzoquinone and 0.41 mL of 2,3-dimethyl-1,3-butadiene in a 4.5-mL minibomb without a solvent; the vessel was heated at 110°C for 18 hours. Recrystallization from acetic acid and washing with a little cold methanol resulted in 0.11 g (36%) of 7: m.p. 210.5-213.0°C; ^{1}H-NMR (DMSO-d_6) δ 1.71 (s, 6, 6- and 7-CH_3), 3.04 (s, 4, 5- and 8-H_2), 3.69 (s, 3, 2-OCH_3), 6.32 (s, 1, 3-H), 7.5, 8.5 (br s, 2, 1- and 4-OH); ^{13}C-NMR (DMSO-d_6) ppm 18.6 (q, 6- and 7-CH_3), 30.8, 31.4 (t, 5- and 8-C), 55.8 (q, 2-OCH_3), 97.8 (d, 3-C), 113.4, 121.9, 122.3, 122.6 (s, 4a-, 6-, 7-, and 8a-C), 135.1, 144.7, 146.1 (s, 1-, 2-, and 4-C); MS, m/e (%), 220 (M^+,

54), 205 (11), 175 (12), 174 (13), 173 (100), 145 (14), 133 (10), 115 (12), 91 (12), 69 (18).

5,8-Dihydro-2-Methoxy-6,7-Dimethyl-1,4-Naphthoquinone,[95] **8**

Compound 7 (0.22 g) was added to $FeCl_3 \cdot 6H_2O$ (0.87 g) in 8.7 mL of ethanol at 70°C in a 25-mL, 2-neck, round-bottom flask equipped with a stirring bar, thermometer, and reflux condenser. After reaction for one hour, the product was separated from the reaction mixture by the addition of ice-water, filtered, and recrystallized from ethanol to give 0.081 g (37%) of **8**: m.p. 133.0-135.0°C [lit.[95], m.p. 151-153°]; ^{1}H-NMR ($CDCl_3$) δ 1.72 (s, 6, 6- and 7-CH_3), 3.00 (s, 4, 5- and 8-H_2), 3.81 (s, 3, 2-OCH_3), 5.86 (s, 1, 3-H). The NMR spectrum was not clean, however, and indicated the presence of a small amount of ethoxy compound which may have resulted by ethoxy/methoxy exchange during recrystallization. GC/MS indicated the presence of approximately 4% (based on peak areas) of a compound with molecular weight 234. This would correspond to the ethoxy compound which had undergone aromatization to the more stable quinol form on the GC column.

2-Methoxy-6,7-Dimethyl-1,4-Naphthoquinone,[94] **9**

Methoxy-p-benzoquinone (0.50 g) and 2,3-dimethyl-1,3-butadiene (0.63 mL) were added to 23 mL of glacial acetic acid in a 100-mL, 3-neck, round-bottom flask equipped with a stirring bar, thermometer, and reflux condenser. The mixture was heated at 45°C for 18.5 hours. A chromic acid solution consisting of 1.85 g $Na_2Cr_2O_7 \cdot 2H_2O$ and 0.093 mL of H_2SO_4 in 1.16 mL of H_2O was then added, and the temperature was kept at approximately 67°C for one hour. Upon addition of this mixture to approximately 100 mL of a 50% ice/water mixture, the product precipitated; it was washed several times with cold water and then dried in the dark at room temperature over P_2O_5 in a vacuum desiccator to give 0.56 g (71%)

of **9**: m.p. 166.7-167.0°C [lit.[123], m.p. 167-168°]; ^{1}H-NMR ($CDCl_3$) δ 2.38 (s, 6, 6- and 7-CH_3), 3.89 (s, 3, 2-OCH_3), 6.08 (s, 1, 3-H), 7.78, 7.83 (s, 2, 5- and 8-H), ^{13}C-NMR ($CDCl_3$) ppm 19.9, 20.2 (6- and 7-CH_3), 56.2 (2-OCH_3), 109.3 (3-C), 126.9, 127.4 (5- and 8-C), 128.7, 129.7 (4a- and 8a-C), 142.6, 143.8 (6- and 7-C), 160.0 (2-C), 179.7 (1-C), 184.6 (4-C).

Compound **9** was also obtained through the reaction of 0.20 g 2,6-dimethoxy-p-benzoquinone with 0.20 mL of 2,3-dimethyl-1,3-butadiene in 3.0 mL of glacial acetic acid. The reaction was run in a 4.5-mL minibomb at 115°C for 17.5 hours and followed by oxidation with a chromic acid solution consisting of 0.93 g $Na_2Cr_2O_7 \cdot 2H_2O$ and 0.046 mL of H_2SO_4 in 0.58 mL of H_2O at approximately 67°C for one hour. The product was isolated as just described. A gas chromatogram of the product of this reaction matched that of the product of the above reaction with an additional component identified by GC/MS as tetramethylanthraquinone (compound **14** - see below).

2-Methoxy-6- and 7-Methyl-1,4-Naphthoquinone,[94] **10a** and **10b**

Methoxy-p-benzoquinone (0.50 g) and isoprene (0.54 mL) were added to 23 mL of glacial acetic acid in a 40-mL Diels-Alder pressure tube equipped with a small stirring bar. The pressure tube was placed in an oil bath above an air stirrer and heated at 100°C for 18.5 hours. Treatment with chromic acid and product isolation were identical to those used for **9**. This resulted in 0.39 g (53%) of a mixture of the isomers **10a** and **10b**: ^{1}H-NMR ($CDCl_3$) δ 2.48 (s, 3, 6- or 7-CH_3), 3.90 (s, 3, 2-OCH_3), 6.13 (s, 1, 3-H), 7.44-7.57 (m, 1, 6- or 7-H), 7.85-8.04 (m, 2, 5- and 8-H); ^{13}C-NMR ($CDCl_3$) ppm 21.6, 21.8 (6- and 7-CH_3), 56.2 (2-OCH_3), 109.4, 109.5 (3-C), 126.0, 126.2, 126.5, 126.6 (5- and 8-C), 128.5, 129.5, 130.7, 131.6 (4a- and 8a-C), 133.6, 134.6, 144.0, 145.2 (6- and 7-C), 159.9, 160.1 (2-C), 179.3, 179.8 (1-C), 184.2, 184.5 (4-C).

The isomeric mixture of compounds **10a** and **10b** was also obtained through the reaction of 0.20 g 2,6-dimethoxy-p-benzoquinone with 0.18 mL of isoprene in 3.0 mL of glacial acetic acid. The reaction was run in a 4.5-mL minibomb at 114°C for 18 hours. Oxidation with chromic acid and product isolation were identical to those described above for the production of **9** by the dimethoxy-p-benzoquinone reaction. ^{1}H- and ^{13}C-NMR spectra were identical to those obtained above with the addition of signals which were determined by GC/MS to be due to dimethylanthraquinone (compounds **15a** and **15b** - see below).

5,8-Dihydro-4,6,7-Trimethylnaphthalene-1,2-Diol,[111] **11**

Compound **3**, produced from 1.90 g of 4-methylcatechol as described above, was dissolved immediately in a mixture of 10 mL 2,3-dimethyl-1,3-butadiene in 10 mL of $CHCl_3$. The resulting solution was kept in the dark at room temperature for 3 hours. Evaporation of the solvent left a brown oil; crystallization was achieved from benzene/petroleum ether (b.p. 50-110°C). The yield was 1.34 g (43% based on 4-methylcatechol). Recrystallization from benzene produced a pinkish-brown product: m.p. 152.5-153.5°C [lit.[111], m.p. 149-151°]; ^{1}H-NMR ($CDCl_3$) δ 1.78 (s, 6, 6- and 7-CH_3), 2.14 (s, 3, 4-CH_3), 3.1-3.2 (br, 4, 5- and 8-H_2), 4.85 (br s, 2, 1- and 2-OH), 6.57 (s, 1, 3-H).

4,6,7-Trimethyl-1,2-Naphthoquinone,[111] **12**

A solution of 0.25 g o-chloranil in 2 mL of anhydrous ether was added to a solution of 0.10 g **11** in 2 mL of anhydrous ether. The orange precipitate which formed immediately was washed three times with cold ether to give 0.081 g (83%) of **12**. Recrystallization from acetone/petroleum ether (b.p. 50-110°C) resulted in orange crystals which decomposed at around 112°C [lit.[111] indicates decomposition at 120°C]; ^{1}H-NMR ($CDCl_3$) δ 2.33, 2.35, 2.36 (s, 9, 4-, 6-, and 7-CH_3), 6.29 (q, 1, J = 1 Hz, 3-H), 7.24 (s, 1, 5-H), 7.87 (s, 1, 8-H); MS, m/e (%), 202

(30), 200 (21), 173 (18), 172 (100), 171 (12), 157 (42), 143 (10), 141 (10), 129 (55), 128 (46), 127 (16), 115 (22), 77 (15), 63 (12), 51 (19), 40 (12), 39 (17). Although MS data indicate a compound with mol. wt. 202, it is likely that this is the aromatized version of **12** which is produced when it acquires hydrogen atoms on the GC column. The IR spectrum of the compound did indicate a quinone carbonyl absorption at 1660 cm^{-1}.

5,8-Dihydro-4,6- and 4,7-Dimethylnaphthalene-1,2-Diol, **13a** and **13b**

The same procedure that was used to produce **11** was employed except that 10 mL of isoprene was used, and the reaction time was 17 hours. Crystallization was achieved from toluene and resulted in 0.92 g (32% based on 4-methylcatechol) of **13**. Recrystallization from toluene resulted in light pink crystals: ^{1}H-NMR (acetone-d_6) δ 1.78, 1.79 (s, 3, 6- or 7-CH_3), 2.05 (s, 3, 4-CH_3), 3.0-3.3 (br, 4, 5- and 8-H_2), 5.55 (m, 1, 6- or 7-H), 6.56 (s, 1, 3-H), 7.30 (br s, 2, 1- and 2-OH); MS, m/e (%), 190 (M^+, 100), 175 (44), 171 (13), 161 (15), 158 (17), 157 (97), 143 (14), 129 (65), 128 (33), 127 (13), 115 (22), 91 (10). Several of the ^{13}C-NMR signals were close together in the aromatic region and were therefore difficult to assign; signals were observed to occur in pairs, however, indicating that a mixture of isomers was produced.

2,3,6,7-Tetramethylanthraquinone, **14**

Compound **14** was obtained as a by-product of several reactions; it was not isolated. The highest yield was obtained through the reaction of 2,6-dimethoxy-p-benzoquinone with 2,3-dimethyl-1,3-butadiene to produce **9** (see above). Evidence for **14** was obtained through GC/MS: MS, m/e (%), 264 (M^+, 100), 249 (38), 236 (12), 221 (27), 193 (14), 191 (13), 178 (17), 103 (10), 40 (13).

2,6- and 2,7-Dimethylanthraquinone, **15a** and **15b**

Compounds **15a** and **15b** were obtained as by-products of the reaction between 2,6-dimethoxy-p-benzoquinone and isoprene to give compounds **10a** and **10b** as described above. They were the only product when the same reaction was run under more severe conditions: 0.20 g of 2,6-dimethoxy-p-benzoquinone and 0.30 mL of isoprene were added to 3.0 mL of glacial acetic acid in a 4.5-mL minibomb and heated at 180°C for 24 hours. This was followed by oxidation with chromic acid and precipitation of the product with ice/water as described above. The yield of this reaction was estimated at 25-30%: ^{1}H-NMR ($CDCl_3$) δ 2.52 (s, 3, 2- and 6- or 7-CH_3), 7.55 (d with fine splitting, 1, J = 8 Hz, 3- and 6- or 7-H), 8.07 (s with fine splitting, 1, 1- and 5- or 8-H), 8.16 (d, 1, J = 8 Hz, 4- and 5- or 8-H); MS, m/e (%), 236 (M^+, 100), 221 (32), 208 (26), 207 (12), 193 (14), 179 (16), 178 (26), 165 (53), 89 (27), 76 (10), 63 (15). The additional splitting observed in the ^{1}H-NMR spectrum and the nature of the behavior of isoprene in the formation of the isomeric mixture of compounds **10a** and **10b** is taken as evidence for the formation of an isomeric mixture of compounds **15a** and **15b**. This was confirmed when recrystallization from methanol resulted in partial separation of the product into two sets of crystals, noticeably different in appearance and melting point.

Compounds **15a** and **15b** were also obtained through the reaction of the isomeric mixture of 2-methoxy-6- and 7-methyl-1,4-naphthoquinone (compounds **10a** and **10b**). The naphthoquinone mixture (0.100 g) which had been obtained through the reaction of methoxy-p-benzoquinone and isoprene was added to a 4.5-mL minibomb, followed by 3.0 mL of acetic acid and 0.074 mL of isoprene. The bomb was then sealed and heated at 150°C for 24 hours. At this time the temperature was lowered to 50°C, and a chromic acid solution consisting of 0.46 g $Na_2Cr_2O_7 \cdot 2H_2O$

and 0.023 mL of H_2SO_4 in 0.29 mL of H_2O was added. The temperature was then maintained at approximately 67°C for 1 hour. Reaction yield was 0.022 g (19%).

3-Methoxyphenanthrene-1,4-Quinone,[106] 16

Methoxy-p-benzoquinone (0.20 g) and styrene (0.17 mL) were added to a 4.5-mL minibomb and heated at 110°C for 10 hours. The product of the reaction was recrystallized from methanol to give 0.018 g (5%) of 16: m.p. 153-157°C [lit.[106], 168-169°]; ^{1}H-NMR ($CDCl_3$) δ 3.91 (s, 3, 3-OCH_3), 6.09 (s, 1, 2-H), 7.49-9.50 (6, 5-H - 10-H); ^{13}C-NMR ($CDCl_3$) ppm 56.6 (OCH_3), 107.1 (2-C), 121.7, 127.5, 128.3, 128.6, 130.2, 135.5 (5-C - 10-C), 160.6 (3-C), 185.0 (1- or 4-C); MS, m/e (%), 238 (M^+, 46), 223 (19), 181 (11), 152 (23), 151 (10), 140 (13), 139 (100), 126 (34), 75 (10), 74 (10), 69 (12).

4a,9,10,10a-Tetrahydro-4-Methylphenanthrene-1,2-Quinone, 17

The same procedure that was used to produce 11 was employed except that 10 mL of styrene was used and the reaction time was 20 hours. Crystallization of the oil remaining after solvent evaporation was attempted from benzene/petroleum ether (b.p. 50-110°C) but was unsuccessful. Analysis of the oil by GC/MS, however, indicated that the monoadduct had formed: MS, m/e (%), 226 (M^+, 15), 171 (13), 170 (94), 156 (13), 155 (100), 154 (11), 153 (14), 128 (15), 115 (13), 92 (12), 91 (58), 77 (25), 65 (10), 51 (12).

1,4-Dihydro-2,3,6,7-Tetramethylphenanthrene-9,10-Diol, 18

Immediately following the addition of 0.90 g sodium periodate in 10 mL of distilled water to 0.70 g of acetovanillone dissolved in 10 mL of glacial acetic acid, 10 mL of 2,3-dimethyl-1,3-butadiene was added. The reaction vessel was kept in the dark with stirring for 4 hours. At that time 1 mL of ethylene glycol was added to combine with any unreacted sodium periodate. The red-orange

precipitate which formed was filtered and rinsed twice with cold methanol to give 0.32 g (29% based on acetovanillone) of **18**. Recrystallization was achieved from methanol. Upon heating in a capillary tube it was found that the bright orange color changed to gray at approximately 130°, brown at around 145°, and back to bright orange again beginning at around 170°C. Melting with some decomposition to a dark brown liquid took place at approximately 260°C.

Attempts to analyze **18** were hampered by its reactivity; ^{1}H-NMR ($CDCl_3$) obtained in less than 2 minutes after dissolution showed δ 1.73 (s, 5, 6- and 7-CH_3), 2.26, 2.32 (s, d, 7, 2- and 3-CH_3), 2.9-3.1 (br, 4, 5- and 8-H_2), 7.10, 7.51 (s, 2, 9- and 10-OH), 7.72, 7.76 (s, 2, 1- and 4-H). Although the integration is not correct for the methyl groups, it is very likely that this is due to the fact that the compound had already started conversion to the fully aromatized phenanthrenequinone. After a few minutes in an NMR tube, **18** turned to an insoluble gel; after standing for two days, however, the solution became clear again and an NMR spectrum could be obtained. This spectrum was virtually identical to that of **19** (see below). MS, m/e (%), showed 268 (M^+, 26), 264 (45), 236 (100), 235 (29), 221 (46), 207 (30), 193 (30), 178 (36), 165 (25). Here again, some conversion to the phenanthrenequinone (mol. wt. 264) is likely.

2,3,6,7-Tetramethylphenanthrene-9,10-Quinone, **19**

Compound **18** (0.10 g) was dissolved in 10 mL of glacial acetic acid in a 2-neck, 25-mL, round-bottom flask. It was then oxidized and isolated as described above, using a chromic acid solution consisting of 0.93 g $Na_2Cr_2O{\cdot}2H_2O$ and 0.046 mL of H_2SO_4 in 0.29 mL of H_2O to give 0.042 g (43%) of **19**: m.p. 250-254°C (with some decomposition); ^{1}H-NMR ($CDCl_3$) δ 2.27 (s, 6, 2- and 7-CH_3), 2.35 (s, 6, 3- and 6-CH_3), 7.55 (s, 2, 4- and 5-H), 7.78 (s, 2, 1- and 8-H).

1,4-Dihydro-2,6-, 2,7-, 3,6-, and 3,7-Dimethylphenanthrene-9,10-Diol, **20**

The procedure employed to form **20** was identical to that used to produce **18** except that 10 mL of isoprene was used instead of 10 mL of dimethylbutadiene; raw yield was 0.14 g (14% based on acetovanillone). The same unusual melting behavior observed for **18** was also observed for **20** and is probably indicative of high reactivity and of conversion to other compounds with heating. The fact that changes occurred over a broader temperature range is likely due to the fact that **20** is actually a mixture of four isomers. ^{1}H-NMR ($CDCl_3$) obtained shortly after dissolution showed δ 1.83 (s, 3, 6- or 7-CH_3), 2.39, 2.45 (s, d, 3, 2- or 3-CH_3), 2.9-3.3 (br, 4, 5- and 8-H_2), 5.55 (m, 1, 6- or 7-H), 7.2-8.0 (m, 5, aromatic H and OH). MS, m/e (%), showed 242 (14), 240 (M^+, 46), 236 (35), 225 (25), 208 (100), 207 (29), 195 (20), 193 (20), 179 (47), 178 (47), 165 (78), 152 (25), 89 (32), 76 (23), 40 (15).

2,6-, 2,7-, and 3,6-Dimethylphenanthrene-9,10-Quinone, **21**

Compound **20** was oxidized to **21** with chromic acid by following the same procedure described above for the oxidation of **18** to **19**. From 0.135 g of **20**, 0.093 g (70%) of **21** was obtained: ^{1}H-NMR ($CDCl_3$) δ 2.39 (s, 2, 2-, and 7-CH_3), 2.46 (s, 4, 3- and 6-CH_3), 7.1-8.0 (m, 6, aromatic H).

Reaction of Compound **5** with 2,3-Dimethyl-1,3-Butadiene

Immediately following the addition of 0.64 g of sodium periodate in 7 mL of distilled water to 0.50 g of α-methylvanillyl alcohol dissolved in 7 mL of glacial acetic acid, 7 mL of 2,3-dimethyl-1,3-butadiene was added. After 1 minute, 1 mL of ethylene glycol was added to combine with any unreacted sodium periodate. The reaction was then allowed to proceed in the dark with stirring.

Two reaction temperatures and times were used. The reaction at room temperature was run for 3 hours. At that time the reaction mixture was extracted with $CHCl_3$ (3 x 50 mL), and the extract was washed with a saturated $NaHCO_3$ solution (2 x 50 mL), washed with distilled water (3 x 50 mL), and dried briefly over anhydrous Na_2SO_4. The solvent was then evaporated under reduced pressure; residual water was removed through the use of several portions of CH_2Cl_2. The resulting brownish red-orange solid was dissolved immediately in hot methanol. Upon cooling, 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (**9**) crystallized; it was washed twice with cold methanol and dried. Recrystallized yield was 0.093 g (14%, based on α-methylvanillyl alcohol); the melting poin. and ^{1}H-NMR spectrum were in agreement with that reported above.

A second reaction was run at 45°C for 18.5 hours. At that time a brown residue was found; 0.034 g was filtered from the reaction mixture: m.p. 205-209°C; MS, m/e (%), 214 (100), 199 (59), 186 (57), 171 (36), 157 (15), 143 (28), 142 (27), 141 (47), 128 (35), 115 (35), 84 (16), 77 (19), 51 (17), 44 (48). The filtrate was oxidized as described above, using a chromic acid solution consisting of 1.85 g $Na_2Cr_2O_7 \cdot 2H_2O$ and 0.093 mL of H_2SO_4 in 1.16 mL of H_2O. The resulting dark red solid was filtered, dried over P_2O_5 in a vacuum desiccator, and dissolved in $CHCl_3$. The $CHCl_3$ was evaporated under reduced pressure and the resulting tar analyzed by GC/MS. A mixture of several components was found; in addition to a peak with a mass spectrum identical to that just described, other major components included 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (**9**), and 2,3,6,7-tetramethylphenanthrene-9,10-quinone (**19**).

Reaction of Compound 5 with Isoprene

The procedure used for the reaction with isoprene was identical to that used for the reaction with dimethylbutadiene; the reaction was run for 4 hours

using 7 mL of isoprene. The ^{1}H-NMR spectrum of the product obtained matched that of a mixture of 2-methoxy-6- and 7-methyl-1,4-naphthoquinone (10) which was reported above. Recrystallized yield was 0.035 g (6% based on α-methylvanillyl alcohol).

Redox Behavior of Compounds

To determine if a redox cycle is likely operating when the compounds synthesized were used as pulping additives, 5.0 mg of each additive and 10.0 mg of glucose were added to 5.0 mL of 1N NaOH in a 16-mL vial and heated under a stream of nitrogen. The color change observed was compared to that of a control sample which contained the additive in NaOH but no glucose. Following heating to approximately 85°C, the solution was allowed to cool in the open air and oxygen was bubbled through it; any color change was again noted. After the addition of another 10 mg of glucose, this procedure was repeated.

As a further test for a redox cycle, the solutions in their oxidized form were analyzed by GC to see if the compounds initially used were still present. This was done by extracting each solution twice with $CHCl_3$, evaporating the extract under a stream of N_2 to approximately one-half its original volume, and analyzing the remaining extract using an OV-17 column and the following temperature program: 1 min at 100°, 100° to 285° at 10°/min, and 10 min at 285°C. Compounds were identified by spiking with a known sample and reanalyzing the extract. In some cases the solution was neutralized with dilute HCl before extraction. Those mixtures in which there was incomplete solubility of the additive were filtered through glass wool in their reduced states before cooling, oxidation, and extraction.

Evaluation of Compounds as Pulping Additives

The effectiveness of the synthesized compounds as pulping catalysts was determined through either or both of two methods. The best evaluation was through an actual pulping reaction; this was carried out for many of the compounds on a laboratory scale. The effectiveness of some additives was also determined by the extent to which they were able to degrade a lignin model compound.

Laboratory Pulping

Evaluation through laboratory pulping was carried out by conducting soda cooks of southern pine. Pulping conditions were identical to those presented in Table 2 above for the isolation of the soda lignin except that they were done on a much smaller scale. Stainless-steel pressure vessels with a maximum capacity of 70 g oven-dry wood were used. Eight cooks were done simultaneously; generally, each batch contained vessels in which anthraquinone was used as an additive and in which no additive was used. Evaluation of each compound was through comparison of yield and kappa number to that obtained using anthraquinone and no additive.

Model Compound Degradation

The lignin model compound used is presented in Fig. 27. As shown in the figure, this model contains a β-aryl ether linkage which is very common in the actual lignin macromolecule. An effective delignification catalyst will readily cleave this linkage, liberating methyl guaiacol. After reaction, gas chromatography was used to determine the extent of model compound degradation by the amount of methyl guaiacol generated.

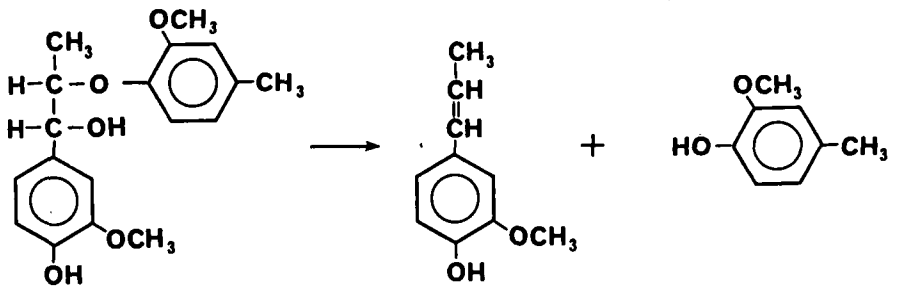


Figure 27. Degradation of a lignin model compound.

The degradations were conducted in 4.5-mL stainless-steel minibombs; generally nine vessels were used at one time. All reactant solutions were added to the vessels with an automatic pipette. The additive (0.300 mg) was first added by accurately weighing approximately 3.0 mg of the additive, dissolving it in enough $CHCl_3$ to get a concentration of 0.300 mg/mL, adding 1 mL of the solution to the bomb, and then evaporating the $CHCl_3$. Amylose (20.0 mg) and cotton linters (20.0 mg) were then added as carbohydrate sources.

The remaining reactants were added to the bombs in a glove bag under a nitrogen atmosphere. An NaOH solution was first prepared by dissolving 1.0500 g of NaOH in deoxygenated, distilled water in a 50-mL volumetric flask and then adding the appropriate amount of make-up water. The lignin model compound solution was then prepared using 47.7 mg of the compound and the NaOH solution in a 10-mL volumetric flask. A glucose solution (additional carbohydrate source) was prepared by dissolving 270.0 mg of glucose in deoxygenated, distilled water in a 50-mL volumetric flask. The lignin model compound solution (1 mL) and glucose solution (2.5 mL) were then added to the bombs; the resulting molar ratio of model compound to glucose to NaOH was 1 to 5 to 35.

The bombs were then sealed, removed from the glove bag, tightened, shaken, and heated at 60° for 30 minutes in a water bath and then at 150° for 30 minutes

in an oil bath. In the oil bath the bombs were mounted on a metal plate which was rotated by means of a chain-drive system and stirring motor. After heating, the bombs were immediately cooled in ice-water. They were then opened and 1 mL of 4-isopropylphenol solution was added. This compound was used as an internal standard in the subsequent GC analysis (molar ratio of 4-isopropylphenol to initial lignin model compound was 1 to 1); the solution was prepared by dissolving 20.4 mg 4-isopropylphenol in 1N NaOH in a 10-mL volumetric flask.

The contents of each bomb was transferred to a 25-mL Erlenmeyer flask and 1 mL dimethylsulfate was added to initiate the methylation of the methyl guaiacol and 4-isopropylphenol. Each mixture was stirred rapidly for 15 min in a loosely stoppered flask. Concentrated ammonium hydroxide (4.5 mL) was then added and the mixture stirred another 15 min to quench the excess dimethylsulfate. Chloroform (2 mL) was added, the mixture was stirred vigorously for 2 min, and the $CHCl_3$ layer was then removed with a disposable pipette, dried over anhydrous Na_2SO_4, and analyzed by GC.

The $CHCl_3$ extracts were analyzed for their methylated methylguaiacol and 4-isopropylphenol contents. The temperature program that was used was 1 min at 100°, 100° to 285° at 10°/min, and 10 min at 285°C.

GENERATION OF METHOXY- AND 2,6-DIMETHOXY-p-BENZOQUINONE

Model compound work indicated that best chance for success in generating an effective pulping catalyst from lignin lay in the production of p-benzoquinones as starting materials for subsequent Diels-Alder reactions. Four oxidative techniques were investigated for their potential in generating methoxy- and 2,6-dimethoxy-p-benzoquinone from lignin and lignin-related compounds; they

were the use of potassium nitrosodisulfonate, hydrogen peroxide, peracetic acid, and electrochemistry.

Evaluation of the effectiveness of the oxidations was generally based on GC analyses of $CHCl_3$ extracts of reaction mixtures. GC retention times and response factors (relative to an internal standard) of most of the compounds involved may be found in Appendix I.

Sources of Lignin and Lignin-Related Compounds

The lignin-related compounds used in this phase of the experimental work are presented in Fig. 28. All compounds except the benzyl alcohols were available commercially[120] and were used as obtained without further purification.

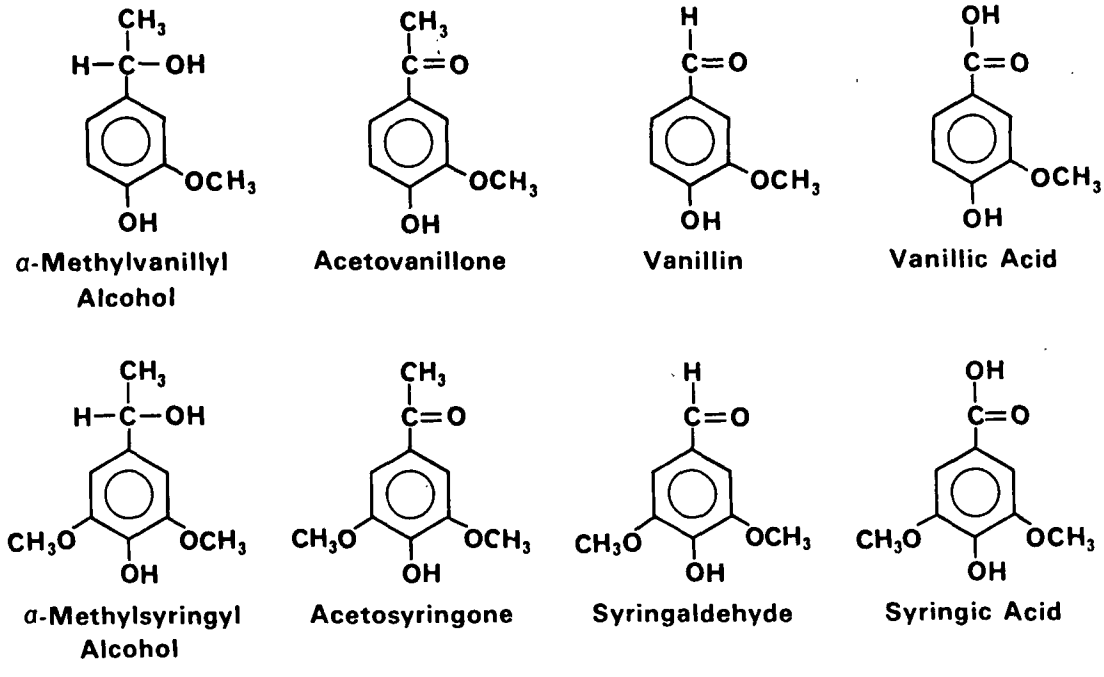


Figure 28. Lignin-related compounds used in the oxidation studies.

α-Methylvanillyl Alcohol[35]

Acetovanillone (35.0 g) was dissolved in 1.06 L of 56% ethanol; sodium borohydride (17.5 g) was then slowly added with stirring. After stirring for 10 hours at room temperature, an additional 5.0 g of $NaBH_4$ was added; stirring was continued for an additional 14 hours. The reaction mixture was then neutralized through the addition of small pieces of dry ice, diluted with approximately 1 L of water, and extracted with ether (5 x 250 mL for each of two batches). After drying over anhydrous Na_2SO_4, the ether was evaporated under reduced pressure, and recrystallization was achieved by dissolving the solid obtained in ethyl acetate and precipitating the product with hexanes; a small amount of solid residue which would not dissolve was filtered from the solution. Recrystallized yield was 26.6 g (75%): m.p. 98-104°C [lit.[35] 100-102°]; ^{1}H-NMR ($CDCl_3$) δ 1.47 (d, 3, CH_3), 1.87 (s, 1, α-OH), 3.89 (s, 3, OCH_3), 4.82 (q, 1, α-H), 5.63 (s, 1, phenolic-OH), 6.83-6.94 (m, 3, aromatic-H).

α-Methylsyringyl Alcohol

The above procedure was repeated using 5.00 g of acetosyringone dissolved in 130 mL of 56% ethanol and 2.70 g of $NaBH_4$; extraction was done with $CHCl_3$. Recrystallized yield was 4.37 g (86%): m.p. 93.5-95.5°C [lit.[124] 95.0-95.5°]; ^{1}H-NMR ($CDCl_3$) δ 1.47 (d, 3, CH_3), 1.99 (s, 1, α-OH), 3.88 (s, 6, OCH_3), 4.81 (q, 1, α-H), 5.52 (s, 1, phenolic-OH), 6.60 (s, 2, aromatic-H).

Hardwood Ethanol Lignin

An organosolv lignin was obtained by cooking air-dry aspen chips (equivalent to 150.0 g oven-dry) in a 2-L pressure vessel containing 750 mL of 95% ethanol and 750 mL of 0.025M HCl. Total reaction time was 135 min with the surrounding oil bath temperature at 156°C; an internal temperature probe indicated that it took approximately 45 min for the contents of the vessel to reach

thermal equilibrium. After reaction, the contents of the vessel were filtered through a 3-L coarse sintered-glass Buchner funnel and washed with two 800-mL portions of 50% ethanol. The pulp was then divided into three approximately equal portions; each portion was added to a Waring Blendor along with 800 mL of 50% ethanol, defiberized for approximately 1 min, filtered through a 3-L coarse sintered-glass Buchner funnel, and washed with three 800-mL portions of 50% ethanol.

The lignin was isolated from the combined wash liquor by evaporating the liquor to approximately one-half volume under reduced pressure to remove most of the ethanol, centrifuging, washing twice with water, and freeze drying. To retain the fine lignin particles, the lignin/water mixture was centrifuged after each wash, and the supernatant obtained after each centrifugation was filtered through a fine sintered-glass Buchner funnel. A portion of the filtered supernatant obtained after the first centrifugation was acidified to a pH of approximately 1 with 4N H_2SO_4 to see if additional lignin could be obtained through acid precipitation. Because it was found that the lignin obtained was less than 2% of the total, acid precipitation was not used in the isolation procedure. The kappa number and fiber and lignin yields obtained in two separate pulping batches are presented in Table 4.

Table 4. The organosolv pulping of aspen with ethanol.

Batch	Fiber Yield (%)	Kappa Number	Lignin Yield (%)
1	55.7	25.1	11.1
2	54.9	23.3	12.7

Low-Molecular-Weight Ethanol Lignin

After the isolation of the first lignin fraction from the second batch, a low-molecular-weight fraction (lmw ethanol lignin) was isolated from the remaining solution. This was done by first reducing the remaining solution, including water which had been used to wash the first lignin fraction, to approximately 250 mL under reduced pressure, generally keeping the temperature below 40°C. This concentrated solution was extracted with $CHCl_3$ (8 x 50 mL); the extract was washed with 50 mL of distilled water, dried over anhydrous Na_2SO_4, and then evaporated.

The solid material which did not dissolve in the $CHCl_3$ (residual lignin) was collected by centrifugation and washed twice with distilled water. The remaining solution, including the wash water from the lmw and residual lignin samples, was evaporated under reduced pressure, again generally keeping the temperature below 40°C, to leave a thick syruplike residue. All three samples were further dried over P_2O_5 in a vacuum desiccator. This procedure resulted in the isolation of 5.8 g lmw ethanol lignin, 0.9 g residual lignin, and 27.5 g pulping residue. GC/MS analysis of a $CHCl_3$ solution of the lmw ethanol lignin showed several peaks; two of these were identified as vanillin and syringaldehyde.

Other Lignin Samples

The origin of the other lignin samples used in the oxidation studies are presented in Table 5.

Oxidation of Lignin and Lignin-Related Compounds

Potassium Nitrosodisulfonate (Fremy's Salt)

The material being investigated was dissolved in 10 mL of ethylene glycol monomethyl ether; in a few cases $CHCl_3$ was used. In general, for model compound

work 1.0 mmol of the compound was used; for comparison of the various lignin samples, 200 mg was used. The reaction flask was cooled to approximately 0°C in an ice bath. Under a stream of nitrogen, potassium nitrosodisulfonate (Fremy's salt, 3.0 mmol) was added to 20.0 mL of a 0.2M KH_2PO_4/K_2HPO_4 buffer solution (pH 6.0) which had also been cooled in an ice bath. The Fremy's salt mixture was then added dropwise to the solution of the material to be oxidized with fairly vigorous stirring, again using a stream of nitrogen to blanket the reaction.

Table 5. Sources of lignin samples used in the oxidation studies.

Sample	Source
Softwood Soda	Isolation described earlier
Hardwood Kraft	Westvaco RLX 4713-3A, Charleston Research Center, North Charleston, SC
Softwood Kraft	Isolated in the thesis work of Furman[33]
Hardwood Sulfite	Reed Lignin D-312-13, Rothschild, WI
Softwood Sulfite	Reed Lignin D-300-2

After the addition of the Fremy's salt, the reaction mixture was removed from the ice bath and allowed to come to room temperature. Total reaction time was generally 2 hours; in a few cases (vanillin, syringaldehyde, and early experiments with ethanol lignin) additional Fremy's salt (1.5-3.0 mmol) was added, and the reaction time was increased to up to 5 hours. After reaction, the mixture was extracted with $CHCl_3$ (4 x 20 mL), and the extract was washed with water (3 x 20 mL), dried over anhydrous Na_2SO_4, and analyzed by GC. A known amount of 4-isopropylphenol was added to the extract for quantitative analysis.

The generation of the two p-benzoquinones was confirmed by MS analysis. With the production of methoxy-p-benzoquinone, MS, m/e (%), showed 138 (M^+, 42), 110 (33), 108 (40), 95 (26), 82 (31), 69 (100), 54 (40), 53 (34), 52 (23), 41 (15), 40 (13), 39 (19); for 2,6-dimethoxy-p-benzoquinone, MS, m/e (%), showed 168 (M^+, 25), 138 (8), 125 (7), 97 (10), 80 (23), 69 (100), 59 (15), 53 (25), 41 (11).

Hydrogen Peroxide

Standardization. A slightly modified procedure of Smith[125] was used. The stock solution was first diluted by a factor of 10; 1.00 mL of this diluted sample was added to 40 mL of 4.0N H_2SO_4. After the addition of 0.2 g Na_2CO_3, which generates CO_2 and purges oxygen from the solution, 20 mL of 1N KI was added; 0.5 mL of 10% ammonium molybdate was added to catalyze the iodine formation. The iodine was then titrated with freshly prepared 0.100N sodium thiosulfate (Acculute). From Eq. (4) and (5), it is clear that 2 moles of sodium thiosulfate are required for each mole of hydrogen peroxide.

$$H_2O_2 + 2\ KI + H_2SO_4 \longrightarrow I_2 + K_2SO_4 + 2\ H_2O \qquad (4)$$

$$2\ Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\ NaI \qquad (5)$$

The stock solution was found to be 10.23M.

Oxidation. The material to be oxidized (1.00 mmol model compound, 0.200 g lignin) was added to 1.00 mL of 1.00N NaOH in an 8-mL vial equipped with a small stirring bar. Hydrogen peroxide (2.50 mL of 1.00M solution) was then added. Aluminum foil was wrapped around the vial to exclude much of the light during reaction; an appropriate reaction time was determined by monitoring the reaction through the use of TLC plates, silica gel, and 15% ethyl acetate/toluene as an eluent.

Following reaction, the mixture was acidified with 10% HCL and extracted with $CHCl_3$ (6 x 10 mL). The extract was dried over anhydrous Na_2SO_4 and analyzed by GC. For quantitative work, a known amount of 4-isopropylphenol was added as an internal standard prior to analysis. Product determinations were based on the retention times of known compounds or through GC/MS analysis. Determinations based on known retention times were checked by spiking the extract with an authentic compound and reanalyzing the sample.

Small amounts of vinylphenols were observed in the reaction mixtures of the alcohols. 2-Methoxy-4-vinylphenol was obtained from α-methylvanillyl alcohol; MS, m/e (%), showed 150 (M^+, 100), 135 (89), 107 (35), 79 (11), 77 (41), 53 (12), 51 (12). 2,6-Dimethoxy-4-vinylphenol was obtained from α-methylsyringyl alcohol; MS, m/e (%), showed 180 (M^+, 100), 165 (42), 137 (29), 122 (15), 91 (11), 77 (16), 65 (10). The oxidation of syringic acid resulted in a small yield of a compound which was not identified; MS, m/e (%), showed 212 (100), 197 (52), 181 (23), 154 (13), 141 (22), 139 (10), 93 (11).

Oxidation of the aldehydes and ketones resulted in good yields of quinones or hydroquinones. Methoxyhydroquinone was produced from both acetovanillone and vanillin; MS, m/e (%), showed 140 (M^+, 100), 138 (5), 125 (85), 97 (59), 69 (12). 2,6-Dimethoxyhydroquinone was generated from both acetosyringone and syringaldehyde; MS, m/e (%), showed 170 (M^+, 100), 168 (33), 155 (58), 127 (50), 112 (25), 80 (15), 69 (58).

Peracetic Acid

Peracetic acid is commercially available from FMC, Industrial Chemicals Division, Downers Grove, IL. The percentage of hydrogen peroxide and peracetic acid in the stock solution was determined both before and after the series of

peracetic acid oxidations was performed, using a slightly modified procedure of Greenspan and MacKellar.[126] There was found to be no change in composition during the course of the experiments.

Ceric Sulfate Standardization.[127] An approximately 0.1M solution was prepared by dissolving 16 g of $Ce(SO_4)_2 \cdot 2(NH_4)_2SO_4 \cdot 2H_2O$ in a solution of 7 mL H_2SO_4 in 125 mL water and then adding an additional 125 mL of water. Approximately 0.35 g of KI was weighed accurately and dissolved in 75 mL of water. Sulfuric acid (5 mL of 18N solution), 3 drops of 0.025M Ferroin indicator, and approximately 22 mL of acetone were then added. The ceric sulfate was titrated until the end-point color change from red to practically colorless persisted for around 30 seconds. Equation (6) shows that 2 moles of ceric sulfate react with 1 mole of potassium iodide.

$$2\ Ce(SO_4)_2 + KI + C_3H_6O \longrightarrow Ce_2(SO_4)_3 + C_3H_5OI + KHSO_4 \qquad (6)$$

Hydrogen Peroxide Standardization. Sulfuric acid (100 mL of 5% solution) was added to a 500-mL Erlenmeyer flask and cooled to around 10°C in an ice bath. Approximately 0.40 g of peracetic acid stock solution was accurately weighed and added; an additional 50 mL of 5% H_2SO_4 (also cooled to approximately 10°) was used to rinse all of the peracetic acid into the flask. Ferroin indicator (3 drops) was then added, and the solution was titrated with standardized ceric sulfate to the disappearance of the pink color; titration was conducted in an ice bath to maintain a temperature below 10°C.

$$H_2O_2 + 2\ Ce(SO_4)_2 \longrightarrow H_2SO_4 + O_2 + Ce_2(SO_4)_3 \qquad (7)$$

Peracetic Acid Standardization. Following the ceric sulfate titration, 10 mL of 10% KI was added. The liberated iodine was then titrated with freshly prepared 0.100N sodium thiosulfate (Acculute) to a starch end-point.

$$C_2H_4O_3 + 2\ KI + H_2SO_4 \longrightarrow C_2H_4O_2 + I_2 + K_2SO_4 + H_2O \quad (8)$$

$$2\ Na_2S_2O_3 + I_2 \longrightarrow Na_2S_4O_6 + 2\ NaI \quad (5)$$

Oxidation. The material to be oxidized (1.00 mmol model compound, 0.200 g lignin) was added to 1.60 mL of glacial acetic acid in an 8-mL vial equipped with a small stirring bar. Peracetic acid stock solution (0.60 mL, found by the standardization procedure to be 36% peracetic acid and 6.7% H_2O_2) was then added. As in the case of hydrogen peroxide oxidation, aluminum foil was used to exclude light, and an appropriate reaction time was determined through the use of TLC plates. Following reaction, 25 mL of saturated $NaHCO_3$ solution was added to neutralize most of the acid; the mixture was then extracted with $CHCl_3$ (6 x 10 mL), and the extract was dried and analyzed as described above for hydrogen peroxide oxidation.

Oxidation of several of the compounds resulted in the generation of acetoxy- and formoxy-compounds. 4-Acetoxy-2-methoxyphenol was obtained from α-methylvanillyl alcohol and acetovanillone; MS, m/e (%), showed 182 (M^+, 14), 140 (100), 125 (79), 111 (11), 97 (52), 96 (10), 79 (12), 69 (15), 68 (12), 53 (20), 51 (11), 43 (54). 4-Acetoxy-2,6-dimethoxyphenol was obtained from acetosyringone; MS, m/e (%), showed 212 (M^+, 18), 170 (100), 155 (42), 127 (23), 69 (10). Oxidation of vanillin produced 4-formoxy-2-methoxyphenol; MS, m/e (%), showed 168 (M^+, 57), 140 (76), 125 (100), 97 (69), 79 (11), 69 (21), 68 (11), 53 (13), 40 (14).

Two unidentified products resulting from the oxidation of α-methylvanillyl alcohol had the following spectra: MS, m/e (%), 154 (20), 126 (9), 123 (18), 111 (8), 71 (6), 69 (100), 68 (6), 53 (6) and MS, m/e (%), 182 (7), 167 (17), 151 (28), 150 (34), 140 (51), 139 (83), 138 (100), 123 (16), 111 (56), 108 (68),

95 (26), 80 (30), 79 (66), 59 (34), 51 (34), 43 (54). An unidentified compound resulting from the oxidation of syringaldehyde had the following spectrum: MS, m/e (%), 182 (100), 167 (12), 153 (12), 149 (13), 139 (55), 111 (22), 109 (18), 94 (13), 83 (55), 69 (39), 67 (13), 53 (10).

Small yields of two unidentified products were obtained from the oxidation of acetosyringone. One of these had a mass spectrum identical to that of the unidentified compound obtained in the oxidation of syringaldehyde; the other had the following spectrum: MS, m/e (%), 184 (100), 169 (43), 141 (19), 113 (25), 85 (10), 69 (26). The mass spectrum of a small amount of unidentified product obtained in the oxidation of syringic acid was identical to that obtained in the hydrogen peroxide oxidation of this compound.

Electrochemistry

Apparatus. The basic setup for the electrochemical oxidations in this phase of the experimental work was the same as that used before in the oxidation of the soda lignin and is illustrated in Fig. 23. Much of the equipment, however, was different from that used earlier.

The cell used for these oxidations was a 100-mL Model C-600 membrane cell obtained from The Electrosynthesis Co., Inc., East Amherst, NY, with a Dupont Nafion No. 117 membrane. The cell was connected in series with an Electrosynthesis Model 415 potentiostatic controller, supplied by a Model 420X accessory power unit, and an Electrosynthesis Model 640 coulometer equipped with a Model 645 shunt. A Fluke Model 8010A digital multimeter was used to obtain the cell voltage. As described earlier, calibration of the coulometer was periodically checked using known current and resistances.

Working electrodes of copper, nickel, iron, lead, platinum, and graphite were constructed. In general, these consisted of 1-inch square sheets of metal of the highest available purity (at least 99.997%) to which a copper connecting wire was attached by using ECR-4100 pure silver electrically-conductive epoxy adhesive obtained from Formulated Resins, Inc., Greenville, RI. The connecting wire was surrounded by a 1/4-inch glass tube which was attached to the metal sheet with Formulated Resins 16-400 chemically-resistant resin; this resin also covered any of the connecting wire and the silver epoxy bond which remained exposed. The graphite anode was constructed from a 1/4-inch Electrosynthesis GR-12 graphite rod by covering the upper portion of the rod with Teflon tape so that only a 1-inch section remained exposed. The counter electrode consisted of a platinum wire coil; the reference electrode was a Beckman 39417 calomel electrode with a ceramic frit.

Oxidation. Anodes were prepared prior to use by successive polishing with 1.0-, 0.3-, and 0.05-μm Buehler alumina micropolish as a water suspension. A lead dioxide anode was obtained from a polished lead electrode by passing approximately 1 amp/dm^2 through a 30% H_2SO_4 solution for 1 min, reversing the current three times (giving two 1-min anodic treatments and two 1-min cathodic treatments), and finishing with an anodic treatment in which the electrode was removed after 2 min with current still flowing in the circuit.

The cell was first assembled and filled to an appropriate level with the solvent system to be used; 90 mL was generally added to the anode compartment. After purging the solution in the anode compartment with nitrogen and allowing the apparatus to reach thermal equilibrium, the anode was pretreated at an appropriate potential (normally the voltage at which the electrolysis was carried

out) for 10 min. Reactions were run at either room temperature or in an ice bath. Background polarization curves (current vs. potential) were obtained before and after the addition of the substrate and used to help determine the electrolysis potential. Substrate concentration was generally 0.05M.

The electrolysis was monitored by periodically withdrawing and analyzing 2.00-mL samples. Each sample was first diluted with approximately 10 mL of water, and the pH was adjusted to around 3 using a saturated $NaHCO_3$ solution or 5% HCl, as required. Internal standard (0.50 mL of a 4-isopropylphenol solution prepared by accurately weighing approximately 50 mg into a 10-mL volumetric flask and dissolving with $CHCl_3$) was then added, and the mixture was extracted with $CHCl_3$ (5 x 5 mL). The extract was reduced in volume, dried over anhydrous Na_2SO_4, and analyzed by GC.

Two compounds with long retention times were noted in the GC analyses of the reaction mixtures resulting from several of the oxidations of the alcohols. MS analysis of a sample withdrawn during the oxidation of α-methylvanillyl alcohol showed: MS, m/e (%), 168 (17), 153 (31), 152 (51), 151 (100), 150 (55), 137 (19), 135 (48), 125 (13), 120 (11), 119 (14), 107 (15), 93 (24), 91 (22), 77 (20), 65 (12), and 318 (10), 168 (13), 153 (22), 152 (46), 151 (100), 150 (36), 137 (14), 135 (31), 93 (13), 91 (12). The analysis of a sample taken during the oxidation of α-methylsyringyl alcohol showed: MS, m/e (%), 378 (5), 198 (22), 183 (31), 182 (100), 181 (83), 180 (65), 167 (25), 165 (26), 155 (12), 151 (16), 137 (17), 123 (20), 91 (12), 77 (15), and 378 (10), 198 (35), 183 (42), 182 (87), 181 (87), 180 (100), 167 (22), 165 (37), 155 (17), 151 (14), 140 (11), 137 (23), 123 (29), 122 (12), 95 (10), 91 (14), 77 (19).

COMBINED OXIDATION/DIELS-ALDER REACTIONS

Some attempt was made to combine oxidation and Diels-Alder reactions using three oxidative techniques.

Potassium Nitrosodisulfonate (Fremy's Salt)

Combined oxidation/Diels-Alder reactions were generally carried out using 0.400 g of lignin. The procedure used for the oxidation part of the reaction was identical to that described above for oxidations by Fremy's salt alone except that 1.0 mL of diene was added just prior to the addition of the Fremy's salt. Following the 2-hour Fremy's salt reaction time, 25 mL of glacial acetic acid was added, and the temperature was raised to an appropriate level. For reactions with isoprene, the reactants were transferred to a 140-mL stainless-steel pressure vessel which was heated in an oil bath.

Following reaction, the mixture was poured onto ice to precipitate the lignin. The lignin was isolated and washed twice with 250 mL of cold water using centrifugation each time to compact the lignin; the supernatant was filtered through a fine sintered-glass Buchner funnel to prevent the loss of small lignin particles. The lignin was then either freeze dried or transferred to a 25-mL, round-bottom flask with glacial acetic acid for chromic acid oxidation.

Chromic acid oxidation was conducted by adding 0.46 g of $Na_2Cr_2O_7 \cdot 2H_2O$ and 0.023 mL of H_2SO_4 in 0.29 mL of H_2O at 50°C and then raising the temperature to 67°C. To obtain a final lignin product which was not too severely degraded, it was necessary to use 10 mL of acetic acid and a reaction time of 30 min. After reaction, the lignin was centrifuged, washed, and freeze dried as just described.

The liquid obtained after precipitation of the lignin was extracted with $CHCl_3$ (4 x 40 mL), and the extract was washed with saturated $NaHCO_3$ solution (2 x 40 mL) and water (3 x 40 mL), and dried over anhydrous Na_2SO_4; in a few cases the entire reaction mixture was extracted. The extract was then evaporated under reduced pressure, sometimes using CH_2Cl_2 to remove residual water, and analyzed by GC/MS.

Analyses of the $CHCl_3$ extracts of the dimethylbutadiene reactions both before and after chromic acid oxidation gave strong evidence of the production of 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (9); MS, m/e (%), showed 216 (M^+, 100), 201 (35), 188 (24), 187 (44), 186 (20), 145 (30), 130 (21), 129 (28), 128 (30), 118 (30), 117 (43), 115 (16), 91 (20), 88 (38), 77 (10), 75 (30). This compares favorably with the mass spectrum of an authentic sample: 216 (M^+, 100), 201 (28), 188 (17), 187 (44), 186 (20), 145 (11), 130 (19), 129 (10), 117 (38), 115 (31), 91 (10), 77 (10). There was also evidence of the generation of 2,6-dimethoxy-p-benzoquinone.

Analyses of the $CHCl_3$ extracts of the isoprene reactions before and after chromic acid oxidation gave strong evidence of the production of 2-methoxy-6- and 7-methyl-1,4-naphthoquinone (10); MS, m/e (%), showed 202 (M^+, 100), 187 (34), 174 (20), 173 (42), 172 (25), 145 (16), 131 (12), 118 (14), 116 (22), 115 (15), 103 (61), 90 (20), 89 (30), 77 (18), 69 (26), 63 (30). This compares very favorably with the mass spectrum of an authentic sample: 202 (M^+, 100), 187 (34), 174 (18), 173 (41), 172 (33), 145 (10), 131 (10), 118 (10), 116 (37), 115 (32), 103 (59), 90 (14), 89 (29), 77 (24), 69 (18), 63 (20). As found with the use of dimethylbutadiene, there was also evidence of the generation of 2,6-dimethoxy-p-benzoquinone.

One compound, appearing to have a molecular weight of 238, could indicate the formation of the isoprene diadduct; MS, m/e (%), showed 238 (43), 183 (100), 182 (58), 167 (20), 139 (15), 123 (10), 69 (14). This compound appeared as a reaction product before chromic acid oxidation after both 112° and 185°C reactions but was much more predominant at the higher temperature.

Peracetic Acid

The compound to be oxidized (1.00 mmol) was added to 1.60 mL of glacial acetic acid in a 4.5-mL minibomb equipped with a small stirring bar; peracetic acid stock solution was then added. After an appropriate reaction time, the stirring bar was removed, isoprene was added, and the vessel was sealed and heated at 60°C for 30 min and then at 180°C for 24 hours with slow rotation.

Following the reaction with isoprene, 5.0 mL of glacial acetic acid was used to transfer the reaction mixture to a 25-mL, 2-neck, round-bottom flask equipped with a stirring bar and a reflux condenser. A chromic acid solution consisting of 0.93 g $Na_2Cr_2O_7 \cdot 2H_2O$ and 0.046 mL H_2SO_4 in 0.58 mL H_2O was then added, and the oxidation was allowed to proceed for 1 hour at approximately 67°C. Approximately 100 mL of saturated $NaHCO_3$ solution was then used to neutralize most of the acid. The resulting aqueous mixture was extracted with $CHCl_3$ (6 x 20 mL); the extract was dried over anhydrous Na_2SO_4 and reduced to 25 mL. A 10-mL portion of this sample was then analyzed by GC using 4-isopropylphenol as an internal standard.

Hydrogen Peroxide/Diene Reactions

A 0.20-g sample of 2,6-dimethoxy-p-benzoquinone was dissolved in 3.0 mL of 1.0N NaOH in a 4.5-mL minibomb. Isoprene (0.30 mL) was then added, and the bomb was sealed and heated at 60°C for 30 min and then at 180°C for 24 hours with

slow rotation. Glacial acetic acid (3.17 mL) was then used to transfer the reaction mixture to a 25-mL round-bottom flask for chromic acid oxidation as just described above. Following acid neutralization with approximately 40 mL saturated $NaHCO_3$ solution, the mixture was extracted with $CHCl_3$, and the extract was dried, reduced in volume, and analyzed by GC as also just described.

NITROBENZENE OXIDATION[53,128,129]

Nitrobenzene oxidations of selected lignin samples were performed to determine the vanillin and syringaldehyde yields that might be obtained. Experiments with lignin-related compounds had shown that these aldehydes might be good starting compounds for further oxidation to p-benzoquinones.

The lignin sample (30.0 mg), 2.0 mL of 2.00N NaOH, and 0.12 mL of nitrobenzene were added to a 4.5-mL minibomb. The bomb was sealed, preheated at 60°C for 30 min, and then heated in an oil bath with slow rotation at an elevated temperature (140°, 159°, or 179°C) for 2.5 hours.

The contents of each bomb was transferred to a 60-mL separatory funnel; the bomb was rinsed twice with approximately 1.5 mL of 1N NaOH and once with approximately 1.5 mL of water. Excess nitrobenzene and its reduction products were then removed by extraction with $CHCl_3$ (2 x 5 mL), using the $CHCl_3$ to again rinse the bomb. Internal standard (1.00 mL of a 4-isopropylphenol solution prepared by accurately weighing approximately 65 mg into a 10-mL volumetric flask and dissolving it with 1N NaOH) was then added, and the mixture was acidified with 4N HCl to a pH of approximately 3. The mixture was then extracted with $CHCl_3$ (6 x 6 mL); the extract was reduced in volume to approximately 5 mL, dried over anhydrous Na_2SO_4, and analyzed by GC.

In addition to vanillin and syringaldehyde, a relatively large amount of one additional product was often found in the $CHCl_3$ extract. This was identified by GC/MS as azoxybenzene: MS, m/e (%), 198 (M^+, 61), 121 (45), 93 (100), 77 (58), 65 (33), 63 (10), 51 (18), 40 (13).

RESULTS AND DISCUSSION

CATALYST GENERATION BY DIRECT OXIDATION OF LIGNIN

The direct oxidation of lignin is a conceivable one-step pathway to a pulping catalyst. This route was therefore briefly examined using electrochemistry and oxidation with potassium thiophenoxide. As discussed in the Experimental Procedures section, the lignin was isolated from a soda pulping reaction of loblolly pine.

Electrochemically-Oxidized Lignin

The lignin oxidations performed are presented in Table 6. They are grouped according to anode material (copper or nickel) and reaction temperature (20° or 60°C), and are in order of increasing anolyte concentration. In all cases the catholyte consisted of NaOH of the same concentration as the anolyte. Blank runs were made to determine the effect of air oxidation alone. Carbohydrates were removed from sample U1; sample U2 was purified through reprecipitation only.

The last column in Table 6 is a comparison of the infrared (IR) absorption due to carbonyl stretching at 1715 cm^{-1} to that due to aromatic skeletal vibration at 1510 cm^{-1}.[113] It should give some indication of the extent to which the original lignin phenyl-propane units were converted into carbonyl (possibly quinone) structures. The absorption ratios were determined several times for sample U1 to get some idea of the experimental error in the data. A mean value of 0.377 with a standard deviation of 0.028 was obtained.

Comparison of sample U1 with sample U2 suggests that it is valid to use the absorption ratio to compare oxidations of lignins purified by the two different

Table 6. Summary of electrochemical oxidations.

Sample	Source[a]	NaOH (N)	Potential (V vs SCE)	Charge (Coul/g)	Absorption Ratio[b]
Copper at 20°C:					
01a	U1	0.20	0.800	315	0.462
01b	U1	0.20	0.800	381	0.492
02	U1	0.50	0.750	3377	1.333
03	U1	0.50	0.800	3333	1.123
04	U1	1.00	0.750	6267	1.900
05a	U1	1.00	0.800	4000	1.619
05b	U2	1.00	0.800	4000	1.921
Copper at 60°C:					
06	U2	0.50	0.750	2000	1.095
07	U1	0.50	0.750	3031	1.346
08	U2	1.00	0.700	2000	1.165
09a	U1	1.00	0.750	3930	1.957
09b	U2	1.00	0.750	4000	2.067
Nickel at 20°C:					
010	U2	0.50	0.800	825	0.727
011a	U2	1.00	0.800	1178	0.795
011b	U2	1.00	0.800	1495	0.926
Nickel at 60°C:					
012	U2	0.50	0.800	2000	0.949
013	U2	0.50	0.800	3940	1.379
014	U2	1.00	0.800	4000	1.456
015	U2	1.00	0.800	6000	1.929
Blank Runs:					
B1	U2	0.50	24 hours at 20°C		0.451
B2	U2	1.00	24 hours at 20°C		0.456
B3	U2	0.50	6 hours at 60°C		0.494
B4	U2	1.00	6 hours at 60°C		0.419
Unoxidized Samples:					
U1a	U1				0.365
U1b	U1				0.403
U1c	U1				0.344
U1d	U1				0.396
U2	U2				0.391

[a]U1 - Purification through carbohydrate removal.
U2 - Purification through reprecipitation only.
[b]Infrared absorption at 1715 cm^{-1} (carbonyl) compared to that at 1510 cm^{-1} (aromatic skeletal).

methods. Comparison of samples 05a and 05b, however, indicates that the results obtained may depend to at least some extent on the purification method. In any case, it is clear that there is a general trend of increasing carbonyl content with increasing severity of oxidation.

Although absorption ratios were not obtained for the acid-soluble lignin samples, the IR spectra of these samples, as well as those of the acid insoluble samples presented in Table 6, were compared to the spectra of methoxy- and 2,6-dimethoxy-p-benzoquinone. This comparison showed that the oxidized lignin samples lacked the strong absorption band at 1660-1690 cm^{-1} which is characteristic of the quinone carbonyl group.[130] At best, only a slight shoulder was noted in the IR spectra of any of these samples.

Potassium Thiophenoxide-Oxidized Lignin

As described in the Experimental Procedures section, the soda lignin was oxidized with potassium thiophenoxide according to the method of Francis and Reeve.[114,115] This technique has been shown to cause extensive demethylation of lignin samples and could lead to an increase in o-quinone content.

After oxidation, the soda lignin increased in weight by approximately 13%; this probably indicates some take-up of thiophenol. Methoxyl analysis indicated an average methoxyl content of 2.8% for the oxidized lignin as compared to 13.6% for the unoxidized sample. A double sulfur trap was employed in the analytical procedure to help ensure the accuracy of the values obtained. Although the standard deviation in the methoxyl determination for the unoxidized sample was fairly large (4.1 for four determinations), it is clear that the lignin underwent a substantial decrease in methoxyl content upon oxidation.

Evaluation of Catalytic Activity

Lignin samples oxidized electrochemically and by potassium thiophenoxide were tested for possible delignification catalytic activity through laboratory pulping using an additive level of 1%, based on oven-dry wood. Pulp yields and kappa numbers were compared to those obtained when no additive was used and when unoxidized soda lignin was used as an additive. The results obtained are presented in Table 7.

Table 7. Laboratory pulping using oxidized lignin.[a]

Sample[b]	Yield (%)[c]	Kappa Number
04	50.0	85.6
07	50.1	87.3
09b	49.9	85.2
011b	49.7	83.8
013	49.9	85.7
015	50.1	85.3
B2	49.9	84.4
Potassium Thiophenoxide Lignin	48.1	74.6
No Additive[d]	49.2	81.9
Soda Lignin	48.4	80.8

[a]Additive level was 1%, based on oven-dry wood.
[b]Sample designations are the same as those used in Table 6.
[c]Yields are based on oven-dry wood in the pulping reaction.
[d]Data values are mean values of all data acquired during the course of the experimental work; see Tables 10 and 11.

These results indicate that the electrochemically-oxidized lignin samples had no beneficial effect on either yield or delignification. It should be pointed out, however, that with the large number of variables involved in electrochemical oxidation, the best conditions may not have been employed here.

Actually, a great deal of time might be required in order to find reaction conditions which might yield more positive results.

Unlike the electrochemically-oxidized lignin, the thiophenoxide-demethylated lignin appears to have a slightly beneficial effect on delignification. However, additional experiments would have to be carried out in order to determine if this slight effect is statistically significant. To get some indication of the amount of error involved, a statistical analysis of some of the data obtained will be presented later. As will be discussed, the standard deviation in the kappa number obtained when no additive is used is 4.0. If there is a similar error in the value of the kappa number obtained when the potassium thiophenoxide-oxidized lignin is used as an additive, then there is no statistical difference between the two values.

In summary, it is clear that any difference in the catalytic activity of oxidized and unoxidized lignin samples which may exist is slight; therefore, no additional work was done in the area of trying to obtain a pulping catalyst directly by lignin oxidation.

GENERATION AND TESTING OF DIELS-ALDER ADDUCTS OF LIGNIN MODEL QUINONES AS PULPING CATALYSTS

The direct oxidation of lignin was found to be an ineffective method for generating useful pulping catalysts. The second phase of the experimental work (Fig. 22), therefore, involved the generation and testing of lignin model quinones and their Diels-Alder adducts. The synthesis of the benzoquinone starting compounds for the Diels-Alder reactions was described earlier in the Experimental Procedures section. These compounds were illustrated in Fig. 24; they include p-quinones which can be obtained from both softwood and hardwood

lignins, and o-quinones with side chains having structural characteristics commonly found in lignin. The selection of the dienes (Fig. 25) was based on reactivity considerations, ease of product characterization, and possible industrial applications.

Synthesis of Diels-Alder Adducts

The experimental procedures used to synthesize the Diels-Alder adducts of the lignin model quinones were also discussed in the Experimental Procedures section. Additional comments on the generation of the adducts presented below are organized according to the starting benzoquinones and dienes. It should be pointed out that little attempt was made to optimize reaction yields. Primary emphasis was placed on the production of the adducts and the testing of these adducts for pulping catalytic activity. The Diels-Alder addition products were illustrated earlier in Fig. 26; a summary of the syntheses used to generate them is presented in Table 8.

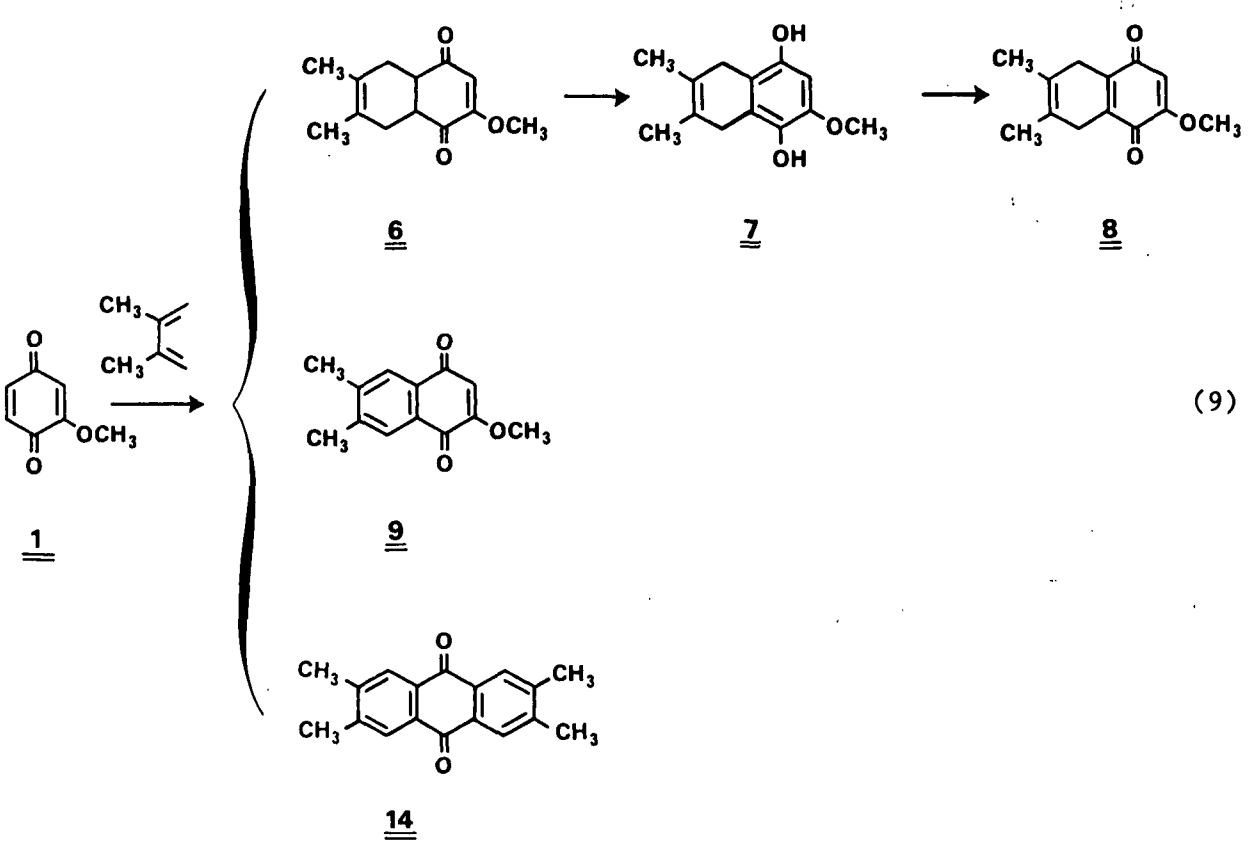
Reactions of Methoxy-p-Benzoquinone

Dimethylbutadiene. Methoxy-p-benzoquinone (1) was prepared by the oxidation of methoxyhydroquinone with lead (IV) oxide.[116] Reaction of 1 with a 50% molar excess of 2,3-dimethyl-1,3-butadiene in methanol[95] resulted in a 24% yield of **6**. Compound **6** has the structural features of a naphthoquinone but is saturated at four of the carbon atoms. Enolization of **6** to a hydroquinone, **7**, (79% yield) was achieved by dissolving **6** in hot glacial acetic acid and adding a few drops of concentrated HCl.[95] Hydroquinone **7** was oxidized to quinone **8** (37% yield) using ferric chloride in ethanol.[95] The amount of brown material obtained in this reaction probably indicates a large number of degradation products and that the oxidation was too severe; this could explain the low yield.

Table 8. Summary of Diels-Alder syntheses.

Starting Quinone	Reactant(s)[a]	Product	Yield (%)
1	1 + DMBD	6	24
	6	7	79
	1 + DMBQ	7	36
	7	8	37
	1 + DMBQ	9	71
	1 + DMBQ	14	--
	1 + Isoprene	10	53
	10 + Isoprene	15	19
	1 + Styrene	16	5
2	2 + DMBD	9	--
	2 + DMBQ	14	--
	2 + Isoprene	10	19
	2 + Isoprene	15	25-30
3	3 + DMBD	11	43[b]
	11	12	83
	3 + Isoprene	13	32[b]
	3 + Styrene	17	--
4	4 + DMBD	18	29[c]
	18	19	43
	4 + Isoprene	20	14[c]
	20	21	70
5	5[d] + DMBD	9	14[e]
	5 + DMBQ	19	--
	5[d] + Isoprene	10	6[e]

[a]See text for reaction details; DMBD = 2,3-Dimethyl-1,3-butadiene.
[b]Based on 4-methylcatechol.
[c]Based on acetovanillone.
[d]Product indicates that reactant was a p-quinone; see text.
[e]Based on α-methylvanillyl alcohol.



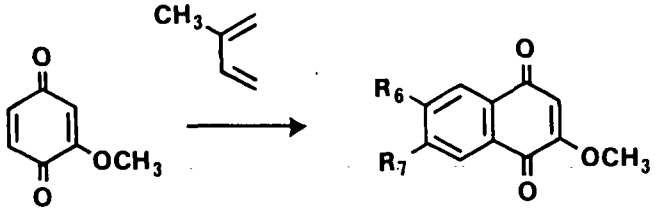
(9)

Compound **8** is just two saturated carbons from being a fully aromatized naphthoquinone. It was found, however, that heating methoxy-p-benzoquinone with 2,3-dimethyl-1,3-butadiene in glacial acetic acid, followed by oxidation with chromic acid,[94] resulted in the direct formation of the naphthoquinone, **9**, in good yield (71%) without isolating any intermediate products. Thus, the conversion of a simple benzoquinone to a naphthoquinone can be done in progressive steps or in a single step; the latter is preferable based on yields.

Attempts to obtain an anthraquinone structure by combining methoxy-p-benzoquinone with two units of diene were largely unsuccessful. When a 2.5 to 1 mole ratio of diene to dienophile was used and the reaction was run at a higher temperature, GC/MS indicated only approximately 3% of the product was the diadduct, tetramethylanthraquinone **14**. As was the case under less severe conditions, the majority of the product was the monoadduct, **9**.

When the same reaction conditions were used without a solvent, only the enolized monoadduct, 7, was obtained (36% yield). This result is significant in that it indicates that following the addition of one unit of the diene, the adduct has a stronger tendency to enolize than to add another unit. The enolized compound is, of course, no longer a dienophile and will not combine with another unit of the diene. A one-step synthesis of an anthraquinone derivative starting with methoxy-p-benzoquinone therefore appears to be difficult.

Isoprene. Reaction of methoxy-p-benzoquinone with isoprene to produce 10a and 10b (53% yield) was achieved in the same way as that used to produce 9. A 1.5 to 1 mole ratio of diene to dienophile was used, and the reaction was run in glacial acetic acid; this was followed by oxidation with chromic acid. The fact that the product was a mixture of the two isomers was learned from ^{13}C-NMR analysis. Although only one compound was apparent by gas chromatography and ^{1}H-NMR, the carbon atoms are sufficiently different that the ^{13}C-NMR spectrum displays closely spaced pairs of signals for all except the methoxy carbons.



1 10

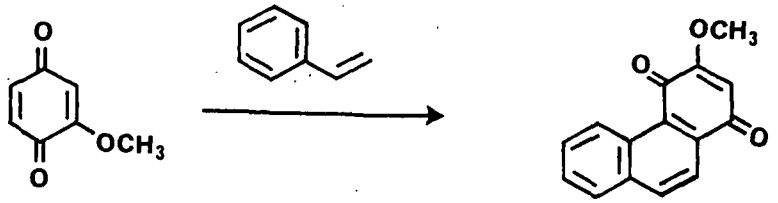
10a, $R_6 = CH_3$, $R_7 = H$

10b, $R_7 = CH_3$, $R_6 = H$ (10)

An experiment was also conducted to see if dimethylanthraquinone (15a and 15b) could be obtained in a two-step reaction in which a second Diels-Alder reaction was performed on the 2-methoxy-6- and 7-methyl-1,4-naphthoquinones initially formed by the combination of methoxy-p-benzoquinone with isoprene. Under

the conditions employed, a 19% yield was obtained for the second step. When this result is considered in light of the 53% yield obtained for the first step, the overall yield is quite low.

Styrene. A complex product mixture (as indicated by gas chromatography) resulted when styrene was reacted with methoxy-p-benzoquinone in acetic acid. The reaction without a solvent,[106] however, was successful, and phenanthrene-quinone 16 was obtained. The low yield (5%), however, indicates that this is probably not a practical industrial reaction.

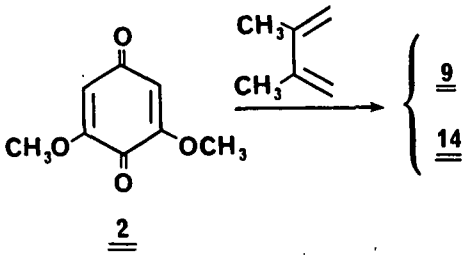


(11)

1 16

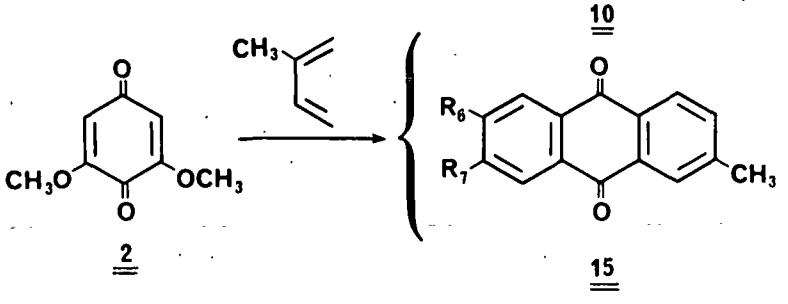
Reactions of 2,6-Dimethoxy-p-Benzoquinone

Dimethylbutadiene. 2,6-Dimethoxy-p-benzoquinone (2) was prepared by the potassium ferricyanide oxidation of 1,3,5-trimethoxybenzene in acetone.[119] Heating a mixture of 2,3-dimethyl-1,3-butadiene and 2,6-dimethoxy-p-benzoquinone (1.5 to 1 mole ratio) in acetic acid, followed by oxidation with chromic acid, gave a product mixture which was approximately 90% naphthoquinone 9 and 10% tetramethylanthraquinone 14. Although a higher percentage of 14 was obtained when the chromic acid step was omitted, the overall yield was much lower; much of the product may have been lost because it did not precipitate. When a 2.5 to 1 mole ratio of diene to dienophile was used, GC/MS indicated that compounds related to 14 became major products, but the yield was again low. Only the starting compound was obtained when the Diels-Alder reaction was attempted in benzene or in no solvent.



2 (12)

Isoprene. Reaction of 2,6-dimethoxy-p-benzoquinone and isoprene in acetic acid using a mole ratio of 1.5 to 1, followed by chromic acid oxidation, resulted in a 19% yield of monomethylnaphthoquinones **10a** and **10b**. As in the reaction with methoxy-p-benzoquinone, the mixture of isomers was detected with ^{13}C-NMR. A small percentage (approximately 6%) of dimethylanthraquinone (**15a** and **15b**) was detected by GC/MS. When the mole ratio was increased to 2.5 to 1 and the reaction was run under more vigorous conditions, the product was entirely dimethylanthraquinone. These results indicate that it is easier to obtain the diadduct from dimethoxy-p-benzoquinone than from methoxy-p-benzoquinone.



2 15 (13)

Because of the high catalytic activity found for dimethylanthraquinone (discussed below), some attempt was made to optimize the yield of this one-step reaction between 2,6-dimethoxy-p-benzoquinone and isoprene. Four runs were made using mole ratios of diene to quinone of 2.5 to 1 and 5 to 1, reaction times of 24 and 36 hours, and a reaction temperature of 180°C. Gas chromatography was

used to analyze for product purity. Best results were obtained when the reaction was run for 24 hours using a mole ratio of 2.5 to 1; the raw yield for this reaction was estimated at 25-30%. Increasing the molar ratio of diene to quinone resulted in the production of several tarry by-products which made product isolation more difficult and did not seem to increase the yield.

Based on the results of this experiment and the two-step synthesis of 15 discussed above, it appears that the one-step synthesis starting with 2,6-dimethoxy-p-benzoquinone is preferable to the two-step reaction. It should be kept in mind, however, that no attempt was made to optimize the yield of either of the steps in the two-step synthetic route.

Styrene. Only the starting material was recovered when 2,6-dimethoxy-p-benzoquinone was heated with styrene, even though the conditions were more vigorous than those employed for the corresponding reaction with methoxy-p-benzoquinone. Apparently the additional methoxyl group is quite effective in blocking the addition of styrene to the compound.

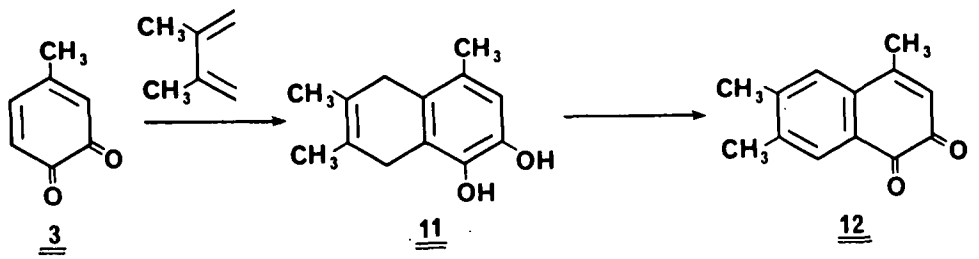
Reactions of 4-Methyl-o-Benzoquinone

It was found that 4-methyl-o-benzoquinone (3) could be obtained by the oxidation of 4-methylcatechol with silver (II) oxide.[35] The yield (14%), however, was small and only small amounts of the compound could be isolated at one time. A second procedure involved the oxidation of 4-methylcatechol with o-chloranil.[121] The yield from this reaction was much higher (64%), but the compound readily degraded after a few minutes under room conditions.

The procedure that was followed for the Diels-Alder reactions, therefore, was to use the o-chloranil oxidation to obtain the 4-methyl-o-benzoquinone, quickly filter and rinse the compound with cold anhydrous ether, and then

immediately combine the o-quinone with the diene. Since the amount of 4-methyl-o-benzoquinone used in the reactions was not determined, yields for the Diels-Alder reactions were based on 4-methylcatechol.

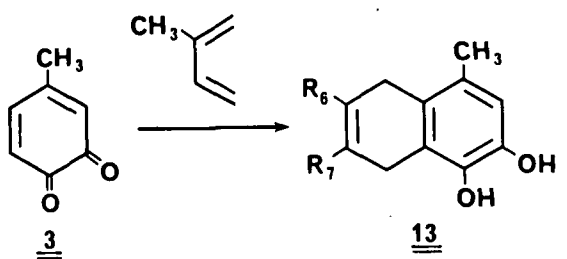
Dimethylbutadiene. Reaction with 2,3-dimethyl-1,3-butadiene was carried out at room temperature for 3 hours in chloroform using a diene to quinone mole ratio of at least 6 to 1 (based on the amount of 4-methylcatechol used).[111] A 43% yield of an o-naphthohydroquinone, 11, was obtained. Apparently the enolized form of the adduct is more stable than the quinone form, and the initially formed adduct is immediately converted to the hydroquinone.



3 11 12 (14)

Oxidation of 11 with o-chloranil in ether resulted in an 83% yield of o-naphthoquinone 12. Although the reaction occurred immediately upon addition of the reactants, recrystallization was difficult and resulted in the loss of most of the product.

Isoprene. Reaction with isoprene was conducted in the same manner as with 2,3-dimethyl-1,3-butadiene but with a longer reaction time (17 hours). This resulted in a 32% yield of a mixture of naphthohydroquinones, 13a and 13b.

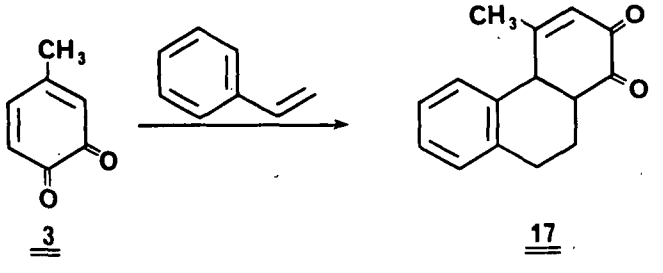


3 13

13a, $R_6 = CH_3$, $R_7 = H$
13b, $R_7 = CH_3$, $R_6 = H$ (15)

The oxidation of **13a** and **13b** to a mixture of o-naphthoquinones was attempted with o-chloranil by following the same procedure that had been used to convert the closely related naphthohydroquinone, **11**, to **12**. Although there was an immediate formation of a brown precipitate, indicative of product formation, the reaction mixture rapidly degraded into a dark brown tar. A second attempt at the reaction, in which the product was dissolved immediately in acetone and recrystallization was attempted from acetone/petroleum ether, also failed to produce the desired product.

Styrene. Reaction with styrene (20 hours) was also conducted in the same manner as with 2,3-dimethyl-1,3-butadiene. Although the product was not isolated, analytical data (GC/MS) indicated that the monoadduct, **17**, had formed.



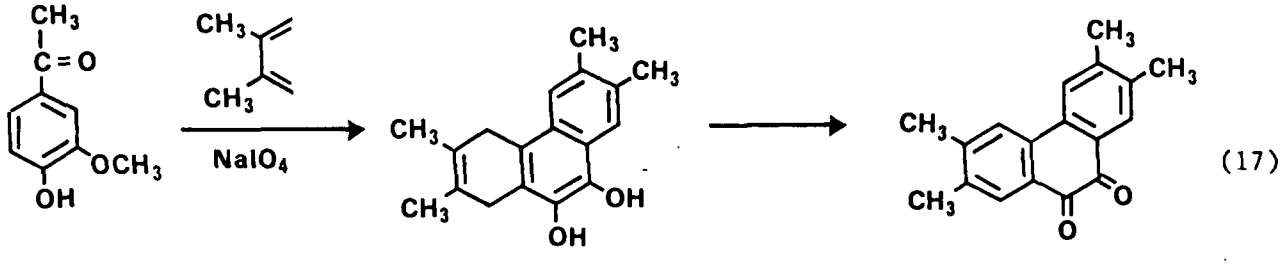
3 **17** (16)

Reactions of 4-Acetyl-o-Benzoquinone

Because of its high reactivity, 4-acetyl-o-benzoquinone (**4**) was not isolated but generated through the sodium periodate oxidation of acetovanillone[122] in the presence of a diene. Because sodium periodate can also react with 4-acetyl-o-benzoquinone, the reaction was monitored by GC and ethylene glycol added after an appropriate reaction time to consume any unreacted sodium periodate.

Dimethylbutadiene. Reaction of 4-acetyl-o-benzoquinone with a large excess of 2,3-dimethyl-1,3-butadiene resulted in a red-orange precipitate which was

identified as the phenanthrene derivative, 18. The maximum yield of precipitate obtained from this reaction (using a time of 4 hours) was 29%. It is likely, however, that the yield is even higher since some of the product remained dissolved in the reaction medium. Unfortunately, the reactivity of this compound in chloroform prevented extraction to obtain additional product and determine the true yield.

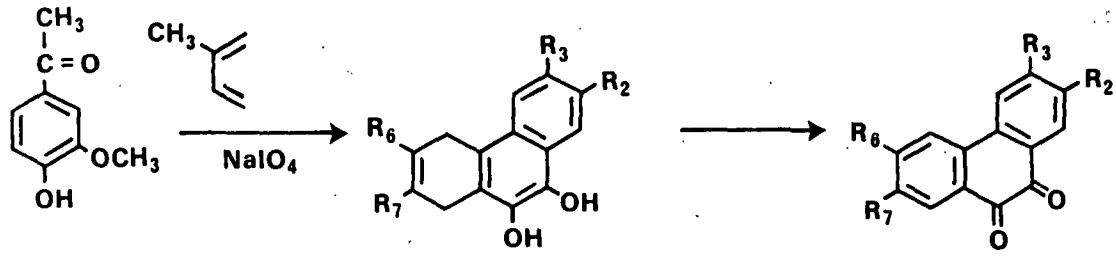


(17)

18 19

Oxidation of 18 with chromic acid resulted in a 43% yield of the tetramethylphenanthrenequinone, 19. The fact that 19 was also obtained by simply adding 18 to chloroform indicates that 18 has a strong tendency to form the fully aromatized phenanthrenequinone.

Isoprene. The reaction of 4-acetyl-o-benzoquinone with isoprene was performed in a similar manner. The product obtained (14% yield) was identified as phenanthrenediol 20 and is most likely a mixture of the four possible isomers, 20a-20d. Oxidation of 20 with chromic acid resulted in a 70% yield of the dimethylphenanthrenequinone, 21, which is again an isomeric mixture.



(18)

20 **21**

20a, $R_2 = R_6 = CH_3$, $R_3 = R_7 = H$

20b, $R_2 = R_7 = CH_3$, $R_3 = R_6 = H$

20c, $R_3 = R_6 = CH_3$, $R_2 = R_7 = H$

20d, $R_3 = R_7 = CH_3$, $R_2 = R_6 = H$

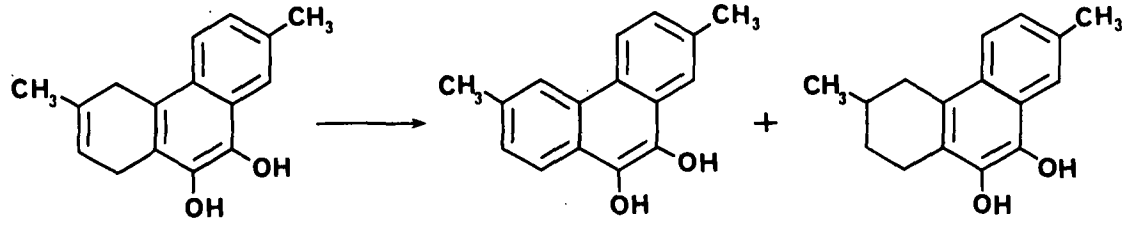
21a, $R_2 = R_6 = CH_3$, $R_3 = R_7 = H$

21b, $R_2 = R_7 = CH_3$, $R_3 = R_6 = H$

21c, $R_3 = R_6 = CH_3$, $R_2 = R_7 = H$

Isolation and analysis of **20** were also hampered by its strong tendency to form the fully aromatized compound. Although the molecular weight of **20** is 240, MS analysis showed fairly prominent signals at m/e 236 and 242. Some conversion to the phenanthrenequinone (mol. wt. 236) is likely. The peak at m/e 242 might be due to the disproportionation reaction indicated by Eq. (19). Analysis of **21** by ^{1}H-NMR indicated a greater amount of isomers in which methyl groups are located at the 3- and 6-positions than at the 2- and 7-positions.

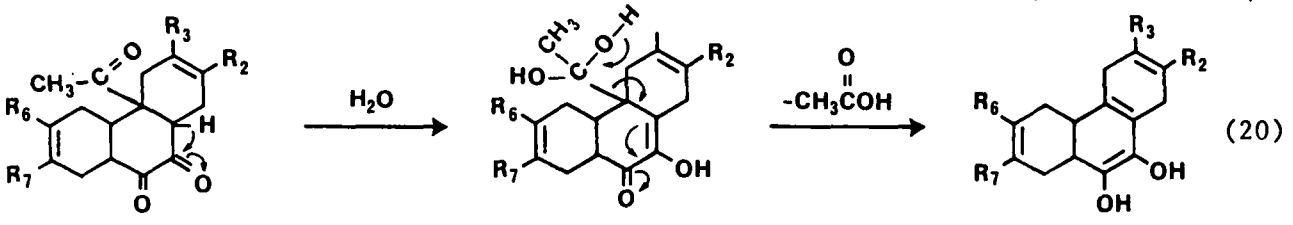
The formation of the phenanthrene derivatives **18-21** is significant in that these compounds can only result through elimination of the acetyl side chain. A similar side chain elimination might be expected if an analogous reaction was



20a

(19)

run using an actual oxidized lignin preparation. A possible mechanism for the side chain loss might involve hydration of the carbonyl group followed by loss of acetic acid as is shown in Eq. (20).



(20)

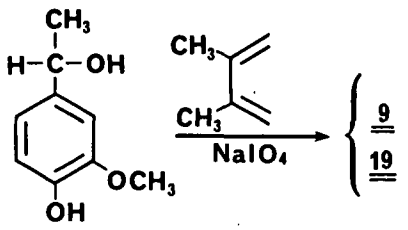
Styrene. An attempt was made to form the Diels-Alder adduct between 4-acetyl-o-benzoquinone and styrene by following the same procedure used for reactions with 2,3-dimethyl-1,3-butadiene and isoprene. The only material isolated from the reaction mixture was the starting compound, acetovanillone. Analysis of the remaining oil by GC/MS also indicated the presence of acetovanillone. Only a trace of material with a molecular weight that corresponded to that of the Diels-Alder adduct was found. Apparently styrene suppresses the formation of the quinone from acetovanillone.

Reactions of 4-(1-Hydroxyethyl)-o-Benzoquinone

Like 4-acetyl-o-benzoquinone, 4-(1-hydroxyethyl)-o-benzoquinone (5) is highly reactive and could not be isolated. It was generated through the reaction of sodium periodate with α-methylvanillyl alcohol in the presence of a diene. Ethylene glycol was again used to consume unreacted sodium periodate, and an appropriate reaction time was determined through the use of gas chromatography.

Dimethylbutadiene. Reaction of the sodium periodate-oxidized α-methylvanillyl alcohol with a large excess of 2,3-dimethyl-1,3-butadiene resulted in a mixture of products; two components were isolated. When the reaction was run at

room temperature for 3 hours, a brown solid was obtained. Recrystallization from methanol resulted, somewhat surprisingly, in a 14% yield of 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (**9**). Although the loss of the 1-hydroxyethyl side chain was anticipated on the basis of the work done with 4-acetyl-o-benzoquinone, the conversion to a p-quinone was not expected.



(21)

However, side chain loss from guaiacyl compounds containing α-hydroxyl groups has been reported during sodium periodate oxidation.[31] A mechanism which could explain the generation of methoxy-p-benzoquinone is presented in Fig. 29.

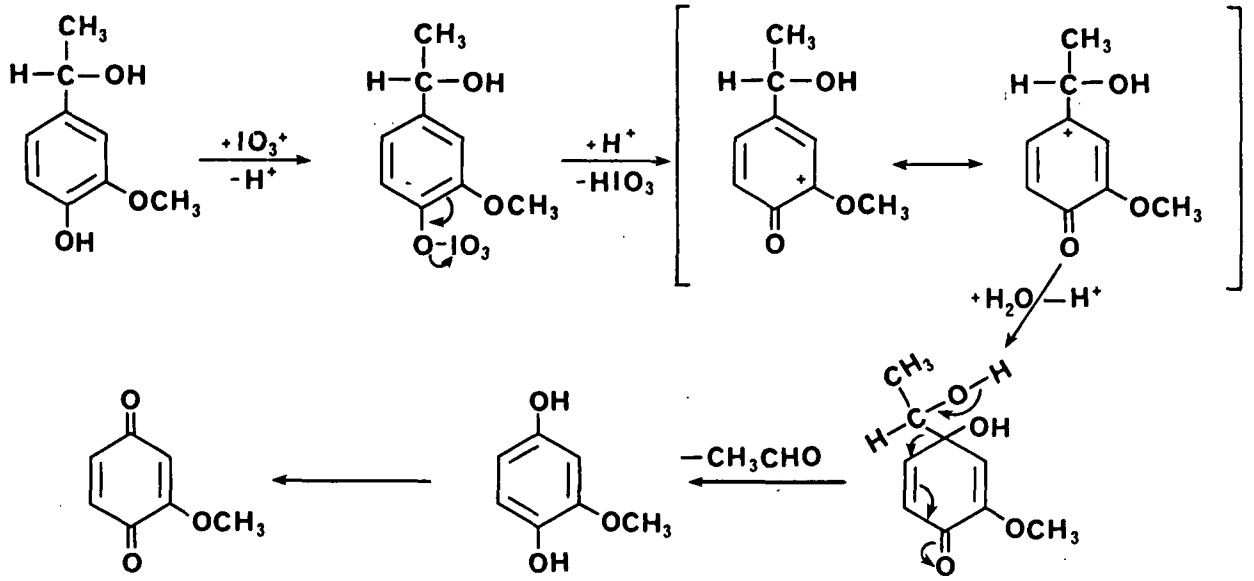


Figure 29. The generation of methoxy-p-benzoquinone during sodium periodate oxidation.

When the reaction time was increased from 3 to 18.5 hours, a small quantity of a brown residue was filtered from the reaction mixture. An NMR spectrum was not obtained because of the reactivity of the material; MS analysis, however, indicated a compound with a probable molecular weight of 214. One possible structure for this compound is 6,7-dimethyl-4-vinyl-1,4-naphthoquinone. This compound could be produced by aromatization of the initially-formed Diels-Alder adduct followed by the loss of water as shown in Fig. 30. The filtrate from the reaction was oxidized with chromic acid and analyzed by GC/MS; the formation of tetramethylphenanthrenequinone **19**, as well as the two compounds mentioned above, was indicated.

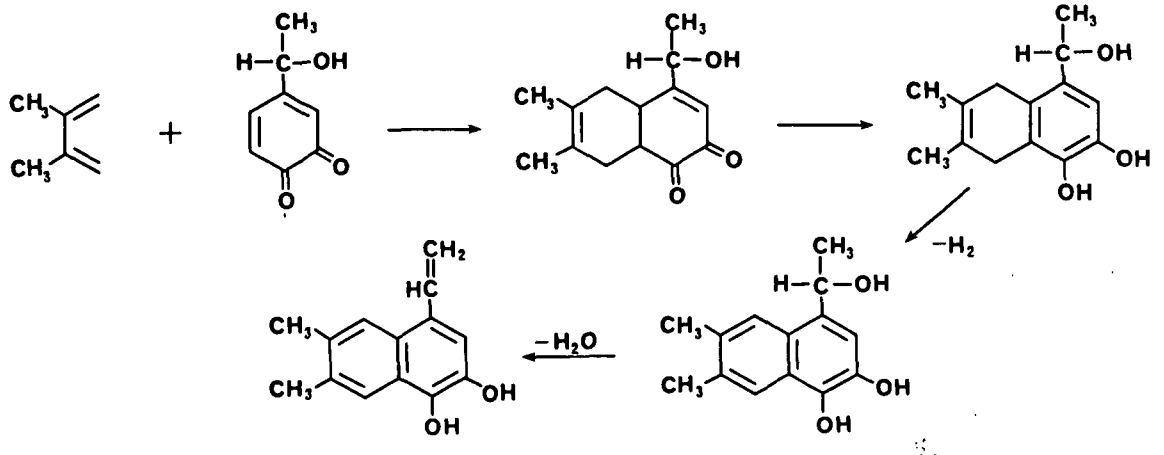
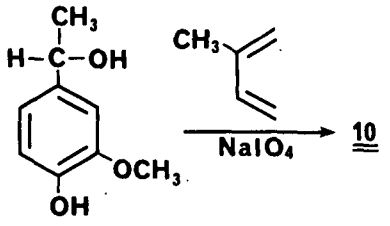


Figure 30. Possible addition reaction of 2,3-dimethyl-1,3-butadiene and 4-(1-hydroxyethyl)-o-benzoquinone.

Isoprene. The reaction with isoprene was performed in a similar manner. With a 4-hour reaction time, a 6% yield of an isomeric mixture of 2-methoxy-6- and 7-methyl-1,4-naphthoquinone (**10**) was obtained. Because of the low yield and the difficulty encountered in isolating products resulting from the dimethylbutadiene reactions, additional work was not performed with isoprene.



(22)

Styrene. An attempt to form the Diels-Alder adduct between 4-(1-hydroxyethyl)-o-benzoquinone and styrene was made by following the same procedure used for reactions with dimethylbutadiene and isoprene. No products could be isolated from the yellow-brown oil obtained. Analysis by GC/MS indicated the presence of two major components which could not be identified. Only a trace of material with a molecular weight that corresponded to that of the Diels-Alder adduct was found.

Redox Behavior of Compounds

To determine whether or not the compounds synthesized might function through a reduction/oxidation cycle such as that proposed for anthraquinone, a two-part investigation was undertaken.

The first part of the study involved noting a color change as the additive was heated with glucose in 1N NaOH under a nitrogen atmosphere and then looking for a second color change as the mixture was allowed to cool in the open air or as oxygen was bubbled through. A color change in glucose would indicate a reduction of the additive; a color change in the presence of oxygen would imply that an oxidation had occurred. A very pronounced color change is observed for anthraquinone; the AQ/glucose solution turns a deep red-orange when heated and is converted back to a yellow color when opened to the atmosphere. Each compound was taken through two complete cycles. The results obtained are summarized in Table 9 and are discussed below. In the second part of the study,

gas chromatography was used to try to detect the starting compound after two reduction/oxidation cycles. These results are also discussed below.

Table 9. Reduction/oxidation colors of various additives.

Compound	Reduced Color	Oxidized Color
Benzoquinones:		
1	Yellow-brown	Gray-brown
2	Yellow-brown	Brown
3	Brown	Brown
Naphthoquinones:		
6	Brown	Orange
7	Brown	Orange
9	Brown	Red-orange
10	Brown	Red-orange
11	Yellow-brown	Blue-green
13	Yellow-brown	Blue-green
Anthraquinones:		
AQ	Red-orange	Yellow
15	Orange-brown	Yellow
Phenanthrenequinones:		
18	Brown	Orange
19	Brown	Orange
20	Brown	Yellow
21	Brown	Yellow

Benzoquinones

Findings in the literature indicate that benzoquinones are not effective pulping catalysts.[4] The test results from p-benzoquinones 1 and 2, and o-benzoquinone 3 were inconclusive. Although a yellowing effect was noted during the reduction part of the cycle, glucose alone yellows when heated. After two cycles, the starting compounds were not detected by GC analysis.

Naphthoquinones

The p-naphthoquinones and their derivatives, 6, 7, 9, and 10, were tested as well as o-naphthoquinone derivatives 11 and 13; in all cases a definite color cycle was observed. However, the initial color changes observed when several of

these compounds were first dissolved, together with the results obtained with the phenanthrenequinone compounds (see below), suggest that in many cases the original compounds were converted to more fully aromatized forms; the color cycling very likely occurred between oxidized and reduced versions of these aromatized derivatives. Analysis by GC indicated that only in the cases of compounds 9 and 10 were some of the starting compounds detected after cycling.

Anthraquinones

Anthraquinone and the isomeric mixture of dimethylanthraquinones, 15a and 15b, were tested. In both cases a definite color cycle was observed, and the starting compound was found to be the major component of a $CHCl_3$ extract analyzed by GC.

Phenanthrenequinones

Compounds 18, 19, 20, and 21 were analyzed. Like the anthraquinones, definite color cycles were observed. GC analysis, however, showed that compound 19 was obtained after starting with both 18 and 19 and that 21 was obtained after starting with both 20 and 21. The ready conversion of 18 to 19 and 20 to 21 has been discussed above. It is possible that this conversion took place in the chloroform extracts or on the GC column; however, it is also likely that the conversion took place in the sodium hydroxide solution and that the fully aromatized phenanthrenequinones were cycled in all four experiments.

Summary of Results

It is difficult to determine whether or not a redox cycle operates when benzoquinone compounds are used. Color changes were of a yellowing nature and could be due to the glucose. GC analysis did not indicate the presence of the starting compound after completion of the color cycle. Color changes indicate

that a redox cycle does operate for naphthoquinone compounds. Changes observed when the compounds were first dissolved, however, suggest that more aromatized versions of the original compounds cycle rather than the compounds themselves. Only for quinones 9 and 10 did GC analysis indicate cycling of the original compound. Both color changes and GC analyses indicate that anthraquinone and phenanthrenequinone compounds operate in a redox cycle like AQ. It is likely, however, that the fully aromatized phenanthrenequinones rather than their partially hydrogenated derivatives actually cycle between reduced and oxidized forms.

This brief study indicates that most of the higher order quinones and their derivatives have the capability to function in a redox cycle. However, additional criteria must be met before a compound will act as an effective pulping catalyst. The evaluation of the compounds as pulping additives is addressed in the following section.

Evaluation of Compounds as Pulping Additives

Analysis of Error in Experimental Results

It should be emphasized that it was not a goal of this thesis to establish the relative effectiveness of each compound synthesized through individual statistically designed experiments. Compound evaluation was more in terms of a screening nature to identify those compounds which might act as effective catalysts. Once these potentially good materials were identified, more detailed experiments were carried out.

It is possible to get a fairly good idea of the amount of error involved in the laboratory pulping experiments, however, by comparing the data obtained for experiments which were repeated several times. Table 10 shows the kappa numbers

and yields obtained when AQ was used at the 0.1% addition level (based on oven-dry wood) in four separate experiments and when no additive was used in six experiments. Reaction conditions were identical to those presented earlier in Table 2. Included in the table are the mean values and standard deviations for each set of data.

Table 10. Error analysis in pulping experiments.

	Anthraquinone[a]		No Additive	
	Kappa No.	Yield (%)[b]	Kappa No.	Yield (%)[b]
			83.5	49.8
			79.1	48.2
	37.1	45.4	86.4	48.2
	36.5	46.0	75.3	48.8
	38.5	45.7	83.4	49.4
	36.2	45.9	83.4	50.5
Mean	37.1	45.8	81.9	49.2
Std. Dev.	1.0	0.3	4.0	0.9

[a]Addition level was 0.1%, based on oven-dry wood.
[b]Yields are based on oven-dry wood in the pulping reaction.

These data indicate that at the 95% confidence level, when AQ is used as an additive at the 0.1% addition level, a kappa number of 37.1 ± 1.6 and a pulp yield of 45.8 ± 0.5 is obtained; when no additive is used, a kappa number of 81.9 ± 4.2 and a pulp yield of 49.2 ± 0.9 is obtained.

Similar errors (4-5% in kappa number, 1-2% in yield) might be expected when other additives are used and when these additives are compared to each other as a group. The errors discussed above include errors both between batches of experiments and between individual pulping reactors within batches. In many of the tables which follow, the data were obtained only from reactors from the same batch; error in these data might therefore be expected to be less than the errors calculated above.

In the model degradation experiments, the variation in experimental results was larger than in the laboratory pulping experiments. In general, each experiment was repeated at least once; the mean value and standard deviation for each trial are reported in the data table which follows.

Evaluation of Quinones and Related Compounds

The results obtained in both laboratory pulping and lignin model compound degradations are presented in Table 11. By using the relationship that percent lignin is approximately equal to kappa number times 0.15,[131] the total fiber yield from pulping was separated into its lignin and carbohydrate components. Compounds are in the order in which they were discussed above: benzoquinones and naphthoquinones and their derivatives are followed by anthraquinones and phenanthrenequinones and their derivatives.

Table 11 shows that generally there is more variation in the data obtained from the lignin model compound degradation study than from the laboratory pulping experiments (as demonstrated in Table 10). As shown by the amount of methylguaiacol produced when no additive was used, another problem with the model compound degradation study was that the model had a strong tendency to degrade in base alone. Therefore, the laboratory pulping data probably give a better indication of the catalytic potential of the additives.

The effect of the additives on kappa number generally is clear; effect on carbohydrate yield is not as apparent. Pulping conditions evidently were such that the carbohydrate stabilization effect of the additives is not obvious.

As might be expected based on their reactivity in base,[58,116] the benzoquinone compounds were not effective as delignification catalysts. The highly

reactive 4-acetyl- and 4-(1-hydroxyethyl)-o-benzoquinone compounds could not be evaluated; of course, their high reactivity rules out possible use as catalysts.

Table 11. Evaluation of compounds as pulping additives (Pulp Study 1).[a]

Compound[b]		Laboratory Pulping[c] Addition Level (%)	Kappa No.[d]	Yield (%)[e] Lignin	Carbohydrate	Total	Model Degradation % Methyl-guaiacol	Std. Dev.
BQs	1	0.2	78.0	5.6	42.4	48.0	75.9	4.2
	2	0.2	78.6	5.6	42.0	47.6	66.3	1.7
	3	--	--	--	--	--	77.6	5.9
NQs	6	0.2	72.7	5.2	42.7	47.9	78.0	8.2
	7	0.2	67.4	4.8	42.7	47.5	81.2	5.9
	9	0.2	70.3	5.0	42.8	47.8	92.5	0.6
	10	0.2	69.0	5.0	43.2	48.2	86.6	1.5
	11	0.2	77.0	5.6	42.6	48.2	63.6	1.8
	12	--	--	--	--	--	67.9	5.4
	13	0.2	72.5	5.2	42.8	48.0	70.1	--
AQs	15	0.1	31.6	2.2	43.6	45.8	--	--
PQs	16	--	--	--	--	--	74.2	2.5
	18	0.1	66.5	4.6	42.0	46.6	72.9	0.4
	19	0.1	68.3	4.8	42.5	47.3	65.0	6.9
	20	0.1	73.5	5.2	42.3	47.5	71.8	1.4
	21	0.1	74.8	5.4	42.6	48.0	69.5	6.2
None		--	81.9	6.0	43.2	49.2	76.3	1.6
AQ		0.1	37.1	2.5	43.3	45.8	102.3	5.5
AQ		0.2	36.3	2.5	43.2	45.7	--	--

[a]Data values are mean values of all data acquired during the course of the experimental work.
[b]BQs = Benzoquinones; NQs = Naphthoquinones; AQs = Anthraquinones; PQs = Phenanthrenequinones.
[c]Addition levels and yields are based on oven-dry wood in the pulping reaction.
[d]Estimated error in kappa number is 4-5%.
[e]Estimated error in total yield is 1-2%; Lignin Yield = 0.0015 x Kappa No. x Total Yield; Carbohydrate Yield = Total Yield - Lignin Yield.

Some catalytic activity was demonstrated by p-naphthoquinone compounds 6, 7, 9, and 10; this is indicated by both a decrease in kappa number in lab pulping and an increase in methylguaiacol yield in the model degradation study. Because the effect was not outstanding, however, and because of rather low

synthetic yields, compounds 6 and 7 were not further evaluated. Compound 8 was not tested both because of low synthetic yield and because of the purification problem noted earlier.

Because the syntheses of naphthoquinones 9 and 10 were fairly straightforward and yields were reasonably high, these compounds were selected for more detailed evaluation. Naphthoquinones could possibly be used as delignification catalysts if large enough quantities could be produced at a reasonably low cost. Higher levels of additive were used in the second pulping study. The results obtained (Table 12) show that 9 and 10 are somewhat effective catalysts at higher addition levels; the slight trend of increasing carbohydrate yield with increasing addition level is worth noting. To achieve the delignification effect of 0.1% AQ, however, might require the addition of up to 2% of these quinones.

Table 12. Evaluation of 9 and 10 at various addition levels (Pulp Study 2).[a]

Compound - Level (%)	Kappa No.	Yield (%)[b]		
		Lignin	Carbohydrate	Total
9 - 0.1	76.5	5.6	42.8	48.4
0.2	74.9	5.4	43.0	48.4
0.4	71.8	5.2	43.1	48.3
0.8	58.1	4.2	43.8	48.0
None	86.4	6.2	42.0	48.2
AQ - 0.1	37.1	2.5	42.9	45.4
10 - 0.1	68.6	4.9	43.2	48.1
0.2	68.9	5.0	43.8	48.8
0.4	68.8	5.0	43.4	48.4
0.8	62.5	4.6	44.4	49.0
None	75.3	5.5	43.3	48.8
AQ - 0.1	36.5	2.5	43.5	46.0

[a]Addition levels and yields are based on oven-dry wood in the pulping reaction.

[b]Lignin and carbohydrate yields are based on kappa no. - see Table 11.

It should be kept in mind that o-naphthoquinones 11-13 were generated from lignin model quinones rather than from quinones which could actually be produced from lignin. The purpose in testing them for catalytic activity was to determine if quinones of this type had any potential as delignification catalysts. Table 11 shows that o-naphthoquinones 11 and 12 are relatively poor as catalysts. Although the use of 13 lowers the kappa number to 72.5, the effect is far below that resulting from the use of AQ.

Because the tetramethylanthraquinone, 14, was only produced in very small amounts, it could not be tested for catalytic activity. Evaluation of this compound by other researchers[13] showed that its effect as a catalyst is substantially below that of AQ. Table 11 shows, however, that the other AQ derivative, the isomeric mixture of 2,6- and 2,7-dimethylanthraquinone (15), has an outstanding effect as a pulping catalyst. It appears to be even more effective than AQ. Because of these excellent results, 15 was compared to AQ at three levels of addition in a separate study. The results obtained are presented in Table 13.

Table 13. Evaluation of 15 at various addition levels (Pulp Study 3).[a]

Compound - Level (%)	Kappa No.	Yield (%)[b]		
		Lignin	Carbohydrate	Total
AQ - 0.05	41.2	2.9	43.5	46.4
15 0.05	35.2	2.5	44.0	46.5
AQ - 0.10	36.2	2.5	43.4	45.9
15 0.10	31.2	2.2	44.6	46.8
AQ - 0.15	33.3	2.3	43.9	46.2
15 0.15	28.9	2.0	44.7	46.7
None	83.4	6.3	44.2	50.5

[a]Additive levels and yields are based on oven-dry wood in the pulping reaction.

[b]Lignin and carbohydrate yields are based on kappa no. - see Table 11.

This table indicates that the dimethylanthraquinone mixture (DMAQ) is more effective than AQ in both lowering kappa number and increasing yield at all levels tested. In fact, better results were obtained with DMAQ at the 0.05% addition level than were obtained with AQ at the 0.10% level. Although the data obtained are not sufficient to be able to show that DMAQ is twice as effective as AQ on a sound statistical basis, the error analysis presented above, together with the data in Table 13, indicate that DMAQ is superior to AQ as a pulping catalyst.

Like tetramethylanthraquinone, DMAQ has already been evaluated as a pulping additive and has been shown to be slightly inferior to AQ.[13] The experimental conditions used in that study, however, were such that the additives were tested at a much higher level; the effectiveness at very low levels apparently was not observed.

Phenanthrenequinones 16 and 18-21 demonstrated effects similar to naphthoquinones 9 and 10. Compound 17 was not evaluated because it was not isolated. Because the mechanism of formation involves side chain elimination, 18-21 could potentially be produced from lignin. The low yields observed in their generation, however, probably precludes their use as pulping catalysts. It is interesting to note the similarity in results obtained for 18 and 19 and for 20 and 21. As discussed earlier, it is quite likely that pulping conditions are such that diols 18 and 20 are converted into the fully aromatized phenanthrenequinones 19 and 21, respectively, early in the pulping process.

Summary of Results

In general the above results indicate that benzoquinones are not effective additives. Naphthoquinones with o-carbonyl groups and phenanthrenequinones are

somewhat effective, but low synthetic yields probably would prevent their economical use as catalysts. Fully aromatized p-naphthoquinones, 9 and 10, also exhibit some catalytic activity; this finding, together with fairly high synthetic yields, indicates that these compounds might have some potential use as pulping catalysts. The increase in carbohydrate yield with increase in addition level is encouraging. Clearly, the isomeric mixture of 2,6- and 2,7-dimethylanthraquinone stands out as an extremely good additive. Product yield (25-30%) is also respectable and might be increased with further research to optimize reaction conditions.

Overall, then, it appears that best chance of success in generating an effective delignification catalyst from lignin lies in the initial production of p-benzoquinone starting compounds. Diels-Alder reactions can then be used to convert these materials into effective naphthoquinone and anthraquinone compounds.

LIGNIN AND LIGNIN-RELATED COMPOUNDS AS A SOURCE OF METHOXY- AND 2,6-DIMETHOXY-p-BENZOQUINONE

Direct lignin oxidation generally resulted in a material that had no effect as a delignification catalyst. Experiments with lignin model quinones, on the other hand, showed that Diels-Alder adducts of p-benzoquinones could result in compounds with significant catalytic activity. Work was therefore undertaken to find oxidative techniques which would produce high yields of p-benzoquinones from lignin and lignin-related compounds. The lignin-related compounds (illustrated earlier in Fig. 28) include models of both softwood and hardwood lignin, containing α-hydroxyl and α-carbonyl groups, as well as compounds which may be derived from lignin. The use of four oxidative techniques was examined

in some detail: potassium nitrosodisulfonate, hydrogen peroxide, peracetic acid, and electrochemistry.

Potassium Nitrosodisulfonate (Fremy's Salt)

As discussed earlier, recent work by Saá, Morey, and Costa[26] and by Saá, Morey, and Rubido[27] showed that high yields of p-benzoquinones can be produced through the oxidation of p-hydroxybenzyl alcohols, p-hydroxybenzoic acids, and p-hydroxybenzaldehydes with potassium nitrosodisulfonate (Fremy's salt), employing $CHCl_3$ as the substrate solvent.

Ethylene glycol monomethyl ether is water soluble, will readily mix with the Fremy's salt suspension, might provide a greater tendency toward reaction, and is a good lignin solvent. Therefore, ethylene glycol monomethyl ether was selected as a solvent, with the anticipation that the information gained from model compound studies might be more applicable to later work with lignin if the same solvent system was used.

The results obtained from Fremy's salt oxidation of lignin-related compounds in ethylene glycol monomethyl ether are summarized in Table 14; syringyl compounds follow guaiacyl compounds and are in the same order. In many cases several reactions were attempted to try to improve the yield; the best results observed are presented. It should be pointed out that the yields reported were achieved by using an internal standard technique in which the internal standard (4-isopropylphenol) was added after all reaction, extraction, and washing of the extract had been done. Comparison of some of the results with corresponding data presented by Saá, Morey, Costa, and Rubido does, in fact, indicate that some yield loss may have occurred during washing of the extract.

Table 14. Fremy's salt oxidation of lignin-related compounds.

Compound	Product[a]	Yield (%)
α-Methylvanillyl Alcohol	MBQ	79
Acetovanillone	--	0
Vanillin	--	0
Vanillic Acid	MBQ	77
α-Methylsyringyl Alcohol	DMBQ	79
Acetosyringone	DMBQ	3
Syringaldehyde	DMBQ	65
Syringic Acid	DMBQ	77

[a]MBQ = Methoxy-p-benzoquinone; DMBQ = 2,6-Dimethoxy-p-benzoquinone.

The importance of the α-hydroxyl group is clearly evident. High quinone yields were obtained from both the alcohols and the acids. Except for syringaldehyde, the yields from compounds containing α-carbonyl groups were, on the other hand, very low or nonexistent. Rapid conversion to an unstable o-quinone would explain why the oxidation of vanillin does not lead to the desired product. The additional methoxyl group present in syringaldehyde may inhibit reactions at C_5 and lessen the level of undesirable by-products.

The Fremy's salt oxidation of various lignin samples is presented in Table 15. Information on the origin of these samples can be found in the Experimental Procedures section. Work with the model compounds indicated that best results were obtained when the reaction was allowed to proceed at room temperature for approximately 2 hours using a 0.2M, pH 6, potassium phosphate buffer solution of Fremy's salt. The use of ethylene glycol monomethyl ether as the substrate solvent proved to be very successful. The conditions used for the models also seemed to give the best results when used on the ethanol lignin. The same conditions were then applied to the other lignin samples without

further modification. The $CHCl_3$ extraction and internal standard techniques for analysis of the product mixtures were also the same as those used for analysis of the model compound reaction mixtures.

Table 15. Fremy's salt oxidation of various lignin samples.

Sample	Quinone Obtained[a]	Yield (%)
Hardwood ethanol	DMBQ	4
LMW ethanol 1	DMBQ	11
LMW ethanol 2	DMBQ	16
Softwood soda	--	0
Hardwood kraft	DMBQ	4
Softwood kraft	--	0
Hardwood sulfite	DMBQ	1
Softwood sulfite	--	0

[a]DMBQ = 2,6-dimethoxy-p-benzoquinone.

Numerous unsuccessful attempts were made to try to increase the yield of quinone from the sample of ethanol lignin above the 4% initially obtained. Increasing temperature, reaction time, and amount of Fremy's salt used, generally had detrimental effects on the yield.

The oxidations of the two low-molecular-weight samples differed only in the product isolation method. Unlike the rest of the samples, the $CHCl_3$ extract of the mixture obtained from the second reaction was not washed extensively and, consequently, more product was retained in the $CHCl_3$. The result serves to illustrate the point made earlier regarding compound yields and indicates that washing losses may be as high as 25%.

The ethanol, hardwood kraft, and sulfite lignin samples appeared to be very reactive toward Fremy's salt and resulted in deep red solutions. Unlike the ethanol and hardwood kraft reactions, however, the sulfite lignin reactions showed little tendency to produce compounds that could be readily extracted with $CHCl_3$. Possibly, Fremy's salt generates o-quinones from all of the lignins; these structures may remain attached to the lignin matrices and, therefore, are not observed as extracted reaction products.

As can be seen from Table 15, 2,6-dimethoxy-p-benzoquinone was obtained only from the hardwood samples. This finding parallels the finding in the model compound study that syringyl units have a much greater tendency to generate p-benzoquinones than guaiacyl units. The yield from the hardwood kraft sample was actually slightly higher than that obtained from the ethanol lignin sample. The soda lignin appeared to be the least reactive sample, generating little color and indicating no trace of either methoxy- or dimethoxybenzoquinone upon analysis.

Hydrogen Peroxide

The hydrogen peroxide oxidation of each of the lignin-related compounds was generally carried out by using 1 mL of 1N NaOH and 2.5 mL of 1M H_2O_2 with 1 mmol of the compound. The results obtained are presented in Table 16 and represent the best results obtained after several trials. Compounds were identified through GC/MS; yields are again based on an internal standard technique.

In contrast to Fremy's salt oxidation, hydrogen peroxide oxidation of lignin-related compounds gave poor results when the compounds contained α-hydroxyl groups. In the attempted oxidation of the two alcohols, even after

several hours, most of the starting compound remained. Oxidation of α-methylvanillyl alcohol resulted in only a trace of 2-methoxy-4-vinylphenol; similarly, only a small amount of 2,6-dimethoxy-4-vinylphenol was obtained from α-methylsyringyl alcohol.

Table 16. Hydrogen peroxide oxidation of lignin-related compounds.

Compound	Reaction Time (min)	Products	Yield[a] (%)
α-Methylvanillyl alcohol	300	2-Methoxy-4-vinylphenol	[4]
		α-Methylvanillyl Alcohol	93
Acetovanillone	60	Methoxy-p-benzoquinone	1
		Methoxyhydroquinone	77
		Acetovanillone	15
Vanillin	10	Methoxy-p-benzoquinone	2
		Methoxyhydroquinone	95
Vanillic Acid	330	No reaction	
α-Methylsyringyl alcohol	300	2,6-Dimethoxy-4-vinylphenol	[12]
		α-Methylsyringyl alcohol	59
Acetosyringone	120	2,6-Dimethoxy-p-benzoquinone	5
		2,6-Dimethoxyhydroquinone	[38]
		Acetosyringone	31
Syringaldehyde	80	2,6-Dimethoxy-p-benzoquinone	24
		2,6-Dimethoxyhydroquinone	[72]
Syringic Acid	330	Unidentified compound	[7]
		Syringic acid	29

[a]Yields are based on a GC internal standard technique; because authentic samples were not always available, values in brackets are approximations based on a typical response factor of 0.4 for related compounds.

Attempted reactions of the acids also went poorly or not at all. The oxidation of syringic acid resulted in a small yield of a compound which was not identified. The recovery of unreacted syringic acid was low; this is likely due to the fact that the acid has a higher solubility in water than in chloroform and was not fully extracted from the reaction mixture.

On the other hand, high yields of quinone or hydroquinone were obtained from both the aldehydes and the ketones; similar results have been reported in the literature.[34,35] Because hydroquinones may be easily oxidized to quinones, high yields of these compounds are also significant. Methoxyhydroquinone was identified as the major product obtained from the oxidation of both acetovanillone and vanillin. A high yield of 2,6-dimethoxyhydroquinone was obtained from the oxidation of acetosyringone and syringaldehyde.

Hydrogen peroxide oxidations were also attempted on the hardwood ethanol, kraft, and sulfite lignins. The oxidation of each sample was carried out by following the same procedure used for the simpler compounds. Each sample appeared to react to some extent with the hydrogen peroxide; the extracts obtained from both the ethanol and kraft lignin samples were clearly yellow. GC analysis, however, indicated no measurable amounts of either methoxy- or 2,6-dimethoxy-p-benzoquinone.

In agreement with the findings of other researchers,[35-38,124,132] the results of the hydrogen peroxide study indicate that it is unlikely that quinone compounds can be isolated through the direct oxidation of lignin. Quinones are either generated in amounts which are too low for practical use or they are degraded almost as quickly as they are produced.

The lignin samples would be expected to contain a much larger percentage of units containing α-hydroxyl groups than α-carbonyl groups. The low reactivity of α-methylvanillyl alcohol and α-methylsyringyl alcohol implies that like the model compounds, lignin units containing α-hydroxyl groups may yield little, if any, quinones. As in the reactions of the analogous model compounds, perhaps lignin units with α-hydroxyl groups tend to lose water to generate vinylguaiacyl and vinylsyringyl structures which are relatively stable to peroxide attack.

The hydrogen peroxide oxidation of some lignin-derived compounds, however, is more promising. The yields of 2,6-dimethoxy-p-benzoquinone and 2,6-dimethoxyhydroquinone from syringaldehyde appear to be quite good. Using similar reaction conditions, a group of Japanese researchers claim to have obtained a 73% yield of 2,6-dimethoxy-p-benzoquinone from syringaldehyde.[133]

Peracetic Acid

The peracetic acid oxidation of each of the lignin-related compounds was generally carried out by adding 1.6 mL of glacial acetic acid and 0.6 mL of peracetic acid stock solution (shown by analysis to be 36% peracetic acid and 6.7% hydrogen peroxide) to 1 mmol of the compound. The results obtained are presented in Table 17, which again indicates the best, but not necessarily the optimum, results obtained.

Table 17 shows that peracetic acid may be used to obtain p-benzoquinones from compounds which contain either α-hydroxyl groups or α-carbonyl groups. The results obtained with the guaiacyl type compounds are basically in agreement with the findings of other researchers.[39-41] Although little has been reported in the literature on the peracetic acid oxidation of syringyl type compounds, the results obtained in this study show that these compounds are more prone to yield quinone products than their guaiacyl analogs.

4-Acetoxy-2-methoxyphenol was identified in the product mixture resulting from the oxidation of α-methylvanillyl alcohol and acetovanillone. Similarly, a good yield of 4-acetoxy-2,6-dimethoxyphenol was obtained from the oxidation of acetosyringone, and a small yield of 4-formoxy-2-methoxyphenol was obtained from vanillin. Mass spectra of the unidentified products are given in the Experimental Procedures section.

Table 17. Peracetic acid oxidation of lignin-related compounds.

Compound	Reaction Time (min)	Products	Yield[a] (%)
α-Methylvanillyl alcohol	20	Methoxy-p-benzoquinone	1
		4-Acetoxy-2-methoxyphenol	[1]
		Unidentified Compounds	[14]
Acetovanillone	95	Methoxy-p-benzoquinone	3
		Methoxyhydroquinone	4
		4-Acetoxy-2-methoxyphenol	[82]
		Acetovanillone	4
Vanillin	25	Methoxy-p-benzoquinone	13
		Methoxyhydroquinone	3
		4-Formoxy-2-methoxyphenol	[5]
Vanillic Acid	540	No Reaction	
α-Methylsyringyl alcohol	20	2,6-Dimethoxy-p-benzoquinone	30
Acetosyringone	35	2,6-Dimethoxy-p-benzoquinone	13
		4-Acetoxy-2,6-dimethoxyphenol	[19]
		Unidentified Compounds	[9]
		Acetosyringone	5
Syringaldehyde	25	2,6-Dimethoxy-p-benzoquinone	17
		Unidentified Compound	[2]
Syringic Acid	360	2,6-Dimethoxy-p-benzoquinone	3
		Unidentified Compound	[5]
		Syringic Acid	16

[a]Yields are based on a GC internal standard technique; because authentic samples were not always available, values in brackets are approximations based on an estimated response factor of 0.5.

The good yields of the acetoxy- and formoxy-compounds (esters) shown in Table 17 suggest that much higher quinone yields are possible from several of the compounds. The generation of the ester compounds is in agreement with the mechanism presented earlier in Fig. 9; compounds of these types should be easily converted to desirable quinones by (1) hydrolysis and (2) mild oxidation. Thus, it is the combined quinone, hydroquinone, and ester yield that is of significance in the table.

The oxidation of each of the lignin samples was carried out using the same procedure that was used for the model compounds. The fact that quinones were obtained from the alcohols and acids, and in particular the 30% yield of 2,6-dimethoxy-p-benzoquinone from α-methylsyringyl alcohol, indicates that peracetic acid should be capable of generating quinones directly from lignin. Table 18 shows that this is, in fact, the case, but the yields are relatively low.

Table 18. Peracetic acid oxidation of lignin samples.

Sample	Quinone Obtained[a]	Yield (mg, %)
Hardwood ethanol	DMBQ	2.5, 1
LMW ethanol	DMBQ	4.2, 2
Hardwood kraft	DMBQ	3.2, 2
Hardwood sulfite	DMBQ	trace

[a]DMBQ = 2,6-Dimethoxy-p-benzoquinone.

As with the other oxidative techniques used, peracetic acid oxidation is clearly more effective in generating quinones from simple lignin-related compounds than from lignin itself. Based on the findings of this study (and that of Nimz[40]), syringaldehyde stands out as a very good compound for the generation of a quinone which may be subsequently converted to effective pulping additives, such as 2,6- and 2,7-dimethylanthraquinone.

Electrochemistry

A summary of the best results obtained after repeated attempts to electrochemically oxidize several lignin and lignin-related samples is presented in Table 19. The experimental conditions used in these reactions, as well as those which proved to be less successful, are discussed below. Initial work focused

Table 19. Electrochemical oxidation of lignin and lignin-related compounds.

Experiment Number	Anode,[a] Potential[b]	Conditions[c]	Quinone[d] - Yield (%)
Oxidations of α-Methylvanillyl Alcohol:			
1	Pb, 1.8	CH_3CN/1.0M H_2SO_4 (7/1), 3°C	MBQ - 7
2	Pb, 1.80	p-Dioxane/0.67M H_2SO_4 (7/3), 28°C	MBQ - 7
Oxidations of α-Methylsyringyl Alcohol:			
3	Pb, 1.80	CH_3CN/1.0M H_2SO_4 (7/1), 3°C	DMBQ - 21
4	Pb, 1.80	p-Dioxane/0.67M H_2SO_4 (7/3), 28°C	DMBQ - 30
5	Pb, 1.6	DMSO/1.0M H_2SO_4 (7/3), 35°C	DMBQ - 16
6	Pb, 1.7	Acetone/1.0M H_2SO_4 (7/1), 28°C	DMBQ - 39
Oxidations of Syringic Acid:			
7	C, 1.5-2.3	0.1N NaOH, 27°C	DMBQ - 10
8	C, 2.00	0.1N NaOH, pH = 7, 25°C	DMBQ - 5
Oxidation of Syringaldehyde:			
9	C, 2.00	0.1N NaOH, pH = 7, 25°C	DMBQ - 2
Oxidation of Ethanol Lignin:			
10	Pb, 2.00	Acetone/1.0M H_2SO_4 (7/1), 28°C	DMBQ - trace
Oxidation of LMW Ethanol Lignin:			
11	Pb, 2.00	Acetone/1.0M H_2SO_4 (7/1), 28°C	DMBQ - 1

[a] Pb = Lead electrode (lead oxide under reaction conditions); C = Graphite electrode.
[b] Volts relative to a saturated calomel electrode.
[c] Substrate concentration was 0.05M for model compound oxidations; 10 mg/mL was used for lignin oxidations.
[d] MBQ = Methoxy-p-benzoquinone; DMBQ = 2,6-Dimethoxy-p-benzoquinone.

on the oxidation of α-methylvanillyl alcohol and α-methylsyringyl alcohol. Reaction conditions that were found to give good results (high quinone yields) were then applied to the oxidation of lignin.

The electrochemical oxidations that have been reported in the literature[51,59-64] have indicated that quinones or quinone precursors (4-hydroxycyclohexa-2,5-dienones) generally are produced in acidic media using a lead dioxide anode. The majority of the reactions presented in Table 19, therefore, were carried out using these conditions.

The problem with acidic conditions is that lignin is generally not soluble in acid. The use of acetonitrile to promote dissolution of the α-methylvanillyl alcohol was somewhat successful if a large amount of acetonitrile was used; a 7% yield of methoxy-p-benzoquinone was observed in this case (Expt. 1). Oxidation of α-methylsyringyl alcohol under similar conditions produced a good yield (21%) of 2,6-dimethoxy-p-benzoquinone (Expt. 3). When the same conditions were used in an attempt to oxidize a lignin sample, however, neither methoxy- nor 2,6-dimethoxy-p-benzoquinone was obtained.

Attempts to oxidize α-methylvanillyl alcohol under neutral conditions resulted in only traces of methoxy-p-benzoquinone. Unsuccessful trials were made using water/acetonitrile with tetra-n-butylammonium perchlorate as supporting electrolyte, water/acetonitrile with sodium perchlorate, and water/methylene chloride with tetra-n-butylammonium perchlorate. The use of methylene chloride was found to severely corrode the lead dioxide anode.

A few oxidations were run with glacial acetic acid to see if an acid medium could be found in which lignin is soluble. The quinone yield from α-methylvanillyl alcohol in acetic acid was very low, however, and severe corrosion of

the anode resulted. An attempt to generate a quinone from α-methylvanillyl alcohol using a basic medium was also unsuccessful.

The use of ethanol as a solvent was also not effective. When sulfuric acid was used as an electrolyte, GC analysis of a sample withdrawn at the start of the reaction showed that after only a few minutes most of the α-methylvanillyl alcohol starting material had been lost. MS analysis indicated the conversion of the alcohol to its ethyl ether under the acidic conditions employed. Because the mechanism for oxidation to the quinone requires a free benzylic hydroxyl group,[63] the ethyl group effectively blocks the formation of the desired product. When an attempt was made to substitute sodium perchlorate for the acid, there was insufficient conductivity for the electrolysis to be carried out.

Unlike ethanol, p-dioxane proved to be a good substitute for acetonitrile for the oxidation of the simple lignin-related compounds. While the yield of methoxy-p-benzoquinone from α-methylvanillyl alcohol remained at 7% (Expt. 2), the yield of 2,6-dimethoxy-p-benzoquinone from α-methylsyringyl alcohol was increased from 21 to 30% (Expt. 4). This positive development was not, however, carried over in the oxidation of the ethanol lignin sample; no quinone products were generated. Although oxidation of α-methylsyringyl alcohol in dimethyl sulfoxide (DMSO) went smoothly, the yield obtained (16%, Expt. 5) was lower than that which was achieved through the use of other solvents.

Some reference to the use of acetone as a solvent in electrochemical generation of quinones is found in the literature. For example, Erdtman[134] obtained a 30% yield of 2,6-dimethoxy-p-benzoquinone from 1,2,3-trimethoxybenzene using an acidified water/acetone solvent system. A 39% yield of the same quinone was obtained by applying a system similar to Erdtman's in the oxidation

of α-methylsyringyl alcohol (Expt. 6). Applying the same conditions to the oxidation of the lignin sample resulted in a slight trace of this quinone (Expt. 10); a 1% yield was obtained from the lmw ethanol lignin sample (Expt. 11).

The generation of products with apparently high molecular weights (indicated by long GC retention times) was sometimes encountered in the electrochemical oxidations of the alcohols. Although the concentration of these products was generally small at the end of the reaction, they were frequently quite large during the reaction, and their increase seemed to correspond directly with a decrease in the amount of reactant.

Through the use of GC/MS, these high molecular weight compounds were identified as dimers of the starting alcohols. The existence of two closely spaced peaks in the gas chromatograms and identical molecular weights indicated that two distinct ether linkages formed between the two halves of the dimer. The most likely structures for the dimers resulting from α-methylvanillyl alcohol are shown in Fig. 31; corresponding structures can be drawn for the dimers of α-methylsyringyl alcohol.

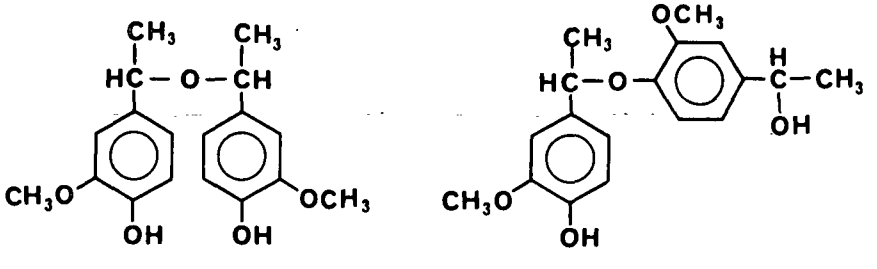


Figure 31. Compounds resulting from the dimerization of α-methylvanillyl alcohol.

The extent to which the formation of these dimers actually interferes with the desired reaction is unclear. Their formation was clearly reversible, and,

as mentioned, they were frequently noted early in the reaction but seemed to be converted back to the starting material as the reaction proceeded to completion.

The use of other oxidative techniques had shown that higher quinone yields may be obtained from lignin-derived compounds, such as vanillin and syringaldehyde, than from lignin itself. Some time was therefore spent in an investigation of the possible electrochemical conversion of lignin-derived compounds to quinones. This work mainly involved the use of syringic acid as the substrate.

Syringic acid was selected for two reasons. First, it may be easily obtained from the oxidation of syringaldehyde which may be obtained directly from lignin. Second, there is some precedence in the literature for the electrochemical decarboxylation of carboxylic acids to yield compounds which might then be further oxidized to quinones.

The oxidation of carboxylates, known as the Kolbe electrosynthesis, is one of the oldest and most useful electrochemical syntheses in organic chemistry.[73] As shown by Eq. (23), it makes possible the preparation of a coupling product from a carboxylate:

$$2\ RCOO^- \longrightarrow R\text{-}R + 2\ CO_2 + 2\ e^- \qquad (23)$$

The mechanism of this reaction can be pictured as an oxidation followed by a decarboxylation of the intermediate acyloxy radical:

$$RCOO^- \longrightarrow RCOO^{\bullet} + e^- \qquad (24)$$

$$RCOO^{\bullet} \longrightarrow R^{\bullet} + CO_2 \qquad (25)$$

Radical coupling may then lead to the final product.

Very early in the use of this synthetic procedure, however, it was noted that several by-products could often be isolated, sometimes as the major components of the reaction mixture. The further oxidation of the radicals, followed by combination of the resulting carbonium ion with a nucleophile in the system, was used to explain the existence of some of these products:

$$R^{\bullet} \longrightarrow R^{+} + e^{-} \qquad (26)$$

$$R^{+} + Nu \longrightarrow R\text{-}Nu^{+} \qquad (27)$$

In general, the dimerization process is successful with radicals which are resistant to further oxidation; these radicals, such as methyl, ethyl, and isobutyl, have ionization potentials greater than about 8 eV.[135] Radicals with lower ionization potentials, such as isopropyl, t-butyl, and benzyl, may undergo further oxidation to carbonium ions.

Other factors, however, are also of great importance in determining the outcome of the reaction.[73] The Kolbe product is favored when using a high current density, a smooth platinum anode, a neutral or slightly acidic solution, methanol or dimethylformamide as a solvent, and low (room) temperatures. The carbonium ion pathway is favored by a low current density, a graphite or lead dioxide anode, an alkaline solution, water or water/pyridine as a solvent, and the addition of ions such as ClO_4^-, HCO_3^-, $H_2PO_4^-$, $SO_4^=$, and F^-.

Most work with the carbonium ion variation of the Kolbe electrosynthesis has involved the oxidation of aliphatic carboxylic acids. Fichter and Meyer,[136] however, were able to convert benzoic acid to benzene. If decarboxylation of syringic acid could be achieved by using an adequate potential, it might be possible to generate 2,6-dimethoxy-p-benzoquinone according to the mechanism

depicted in Fig. 32. The decarboxylation potential would very likely be high enough to further oxidize the hydroquinone to the quinone.

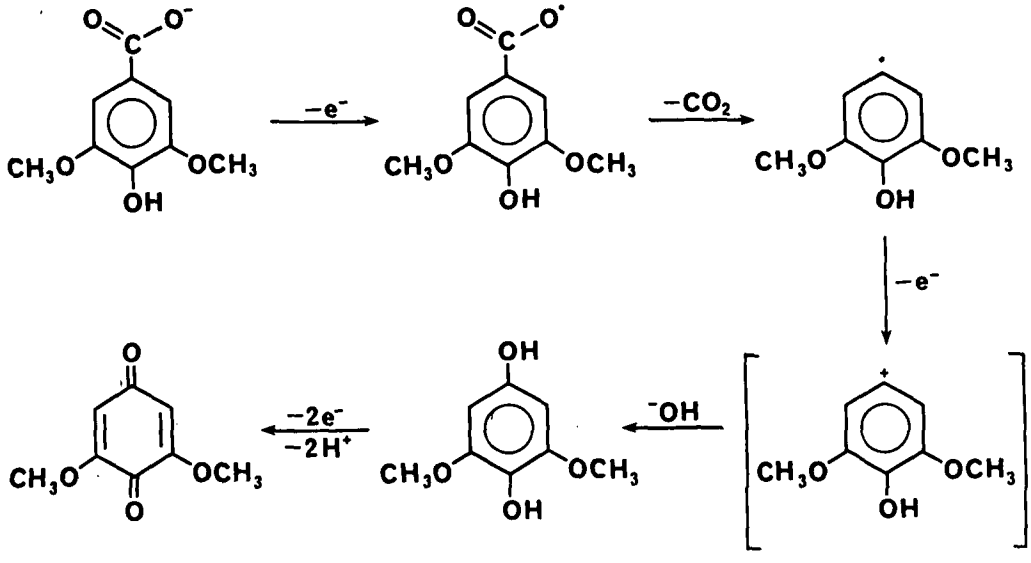


Figure 32. Mechanism for the electrochemical oxidation of syringic acid.

In the first attempt to electrochemically generate 2,6-dimethoxy-p-benzoquinone from syringic acid (Expt. 7), the anode potential was set as high as the equipment would allow, using a cell potential of approximately 37 V. As the conductivity of the solution changed, the anode potential varied over a fairly wide range. It was soon discovered that the conductivity change was due to a decrease in hydroxide ion concentration as the electrolysis proceeded. When this concentration became too low, not only did the conductivity decrease substantially, but the syringic acid precipitated. To restore a reasonable set of reaction conditions, 1N NaOH was added periodically. The 10% quinone yield was very encouraging, however, and the experiment was repeated using an automatic titration device to add NaOH to maintain a constant pH. The best result that was achieved under these more controlled conditions, however, was a 5% quinone yield (Expt. 8).

One attempt was made to oxidize syringaldehyde, using similar reaction conditions (Expt. 9). The reaction proceeded very slowly, and only a 2% yield of 2,6-dimethoxy-p-benzoquinone was obtained. A possible mechanism for this reaction is the oxidation of the aldehyde to the acid, followed by the variation in the Kolbe electrosynthesis depicted in Fig. 32.

Although the direct electrochemical oxidation of lignin gave some positive results, the yields were far below those obtained through the use of other techniques. The results of the oxidation of the lignin-derived compound, syringic acid, were also not highly encouraging. It appears that electrochemical oxidation might be a viable alternative to the use of chemical oxidants, but considerable developmental work might be needed in the experimental conditions in order to get significantly better results. Time might more effectively be spent in efforts to try to optimize the generation of quinone through the use of chemical oxidants which have already been shown to give yields that are much higher.

ONE-STAGE CATALYST GENERATION BY COMBINED OXIDATION/DIELS-ALDER REACTIONS

It is clear that the two steps needed to generate a pulping catalyst from lignin, namely the generation of quinones from lignin or lignin-related compounds, and the conversion of these quinones via a Diels-Alder reaction into naphtho- or anthraquinone compounds, can be carried out. From an economic standpoint, however, it may be advantageous if these two steps can be combined into one operation. Oxidation to quinones in the presence of a diene might also be effective in trapping short-lived quinones, such as o-quinones, and converting them into compounds with catalytic properties.

Potassium Nitrosodisulfonate/Diene Reactions

Appropriate reaction conditions for a combined Fremy's salt oxidation/Diels-Alder reaction were established by first using the model compound, α-methylvanillyl alcohol. After the alcohol was dissolved in ethylene glycol monomethyl ether, 1 mL of 2,3-dimethyl-1,3-butadiene was added just prior to the addition of the Fremy's salt. Following a 2-hour reaction time at room temperature, the temperature was raised to 45°C for 18 hours. Earlier work had shown that under these conditions dimethylbutadiene combines with methoxy-p-benzoquinone to produce a good yield of the Diels-Alder adduct.

A green solid, probably a salt resulting from the presence of Fremy's salt products in the reaction vessel, precipitated along with the desired naphthoquinone in early attempts to follow the Diels-Alder reaction by chromic acid oxidation to fully aromatize the adduct. However, this undesired by-product could be avoided by isolating the Diels-Alder adduct prior to chromic acid oxidation. Through the use of this procedure, a 26% yield of 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (9) was obtained.

After the work with the model compound, the hardwood ethanol lignin sample was selected for reaction; the technique which was just described for α-methylvanillyl alcohol was applied to this sample, using both dimethylbutadiene and isoprene. However, chromic acid was found to severely degrade the lignin, resulting in a low yield of the final product. Reactions were therefore conducted both with and without the chromic acid oxidation step; these reactions are summarized in Table 20.

Table 20. Fremy's salt oxidation/Diels-Alder reaction of ethanol lignin.

Sample	Diene[a]	Diels-Alder Reaction Conditions	Chromic Acid Oxidation	Lignin Recovered (%)
A	DMBD	45°C, 18 h	No	51
B	DMBD	45°C, 18 h	Yes	2
C	Isoprene	112°C, 18 h	No	83
D	Isoprene	112°C, 18 h	Yes	37
E	Isoprene	185°C, 24 h	No	118

[a]DMBD = 2,3-dimethyl-1,3-butadiene.

Basically, the conditions used for the Fremy's salt oxidation were those that had demonstrated success in generating p-benzoquinones from model compounds and from samples of ethanol lignin; conditions used for the Diels-Alder reactions were those that had proven successful in converting p-benzoquinones to naphthoquinones and anthraquinones.

The solutions obtained after precipitation of the lignin were extracted with $CHCl_3$ to determine if quinone structures were, in fact, being generated. In the dimethylbutadiene reactions, GC/MS analysis showed the production of 2-methoxy-6,7-dimethyl-1,4-naphthoquinone (9) as well as partially aromatized versions of the compound. In the isoprene reactions at a lower temperature (112°C), the generation of the mixture of 2-methoxy-6- and 7-methyl-1,4-naphthoquinones (10) was indicated. There was also indication of the production of a compound with mol. wt. 238 which may be the diadduct in a state which is not completely aromatized. This same compound was found in a larger amount in the $CHCl_3$ extract of the reaction mixture resulting from the isoprene reaction at 185°C.

It is interesting to note that 2,6-dimethoxy-p-benzoquinone was also found in most of the extracts and appeared to be more predominant in the extracts of

the mixtures obtained after chromic acid oxidation. This seems to indicate that the Diels-Alder reaction did not go fully to completion. Perhaps more important, the greater concentration found in samples after the chromic acid oxidation may indicate that the quinone is somehow tied up in the lignin - perhaps through some type of charge-transfer complex. An experiment in which a solution of α-methylvanillyl alcohol, containing some ethanol lignin, was oxidized by Fremy's salt also resulted in a reduced yield of methoxy-p-benzoquinone.

The five Fremy's salt-oxidized/Diels-Alder-enhanced ethanol lignin samples were tested for their effectiveness in degrading a lignin model compound. A sample of ethanol lignin itself and a sample which had been oxidized but not further combined in a Diels-Alder reaction were also tested.

Their relative effectiveness, as measured by the amount of methylguaiacol produced, is presented in Table 21. For comparison, the results obtained when anthraquinone (AQ) was used and when no additive was used are also included. Because the effective portion of each lignin sample very likely represents only a fraction of the entire sample, the addition level (3.0 mg) was 10 times that of the AQ level used. This higher addition level permitted the weighing of each lignin sample directly rather than using a $CHCl_3$ solution, as had been done previously.

Although some activity is indicated, in general none of the samples proved to be very effective delignification catalysts. The sample obtained through reaction with isoprene at 112° (sample C) does give some indication of increased activity; when tested at a lower addition level (1.5 mg), however, sample C was not found to be very effective. The data at the bottom of the table show that very little methylguaiacol results from the lignin itself even when there is an effective catalyst (AQ) present.

Table 21. Sample evaluation through lignin model compound degradation.

Sample[a]	Model Degradation Results[b] (% Methylguaiacol)
Ethanol lignin	65.4
Oxidized ethanol lignin	55.4
A	71.2
B	72.6
C	80.2
C (1.5 mg)	73.4
D	72.6
E	73.4
AQ	86.7
None	60.8
Ethanol lignin, no model	4.2
Ethanol lignin + AQ	79.3
Ethanol lignin + AQ, no model	7.0

[a]Sample designations are the same as those used in Table 20. Unless specified otherwise, additive level was 3.0 mg lignin and 0.3 mg AQ.
[b]See Experimental Procedures section for reaction details.

It should be pointed out that although the lignin model compound used in this evaluation was the same one which had been used earlier, the results obtained when AQ was used as an additive and when no additive was used are lower than those obtained in earlier work (Table 11). A possible source of error is a change in the response factor of the GC column employed in the analysis; ^{1}H-NMR analysis of the model compound indicated little degradation since its previous use. Therefore, although the results presented above provide a good comparison of the relative effectiveness of the samples represented, these results should not be compared to those presented earlier for quinones generated from lignin model compounds. To give some indication of the amount of error that might be involved in the data in Table 21, the experiments using AQ and using no additive were repeated. Mean values (presented in the table) of 86.7 and 60.8 with standard deviations of 2.5 and 4.9, respectively, were obtained.

Because the model degradation study indicated that sample C might have some activity as a delignification catalyst, laboratory pulping was also used to evaluate this sample; the results obtained are shown below in Table 22. It is clear from this table that sample C is not an effective pulping catalyst.

Table 22. Sample evaluation through laboratory pulping.

Sample - Level (%)[a]	Kappa No.	Yield (%)[b]		
		Lignin	Carbohydrate	Total
C - 0.75	88.6	6.8	44.3	51.1
AQ - 0.10	36.2	2.5	43.4	45.9
None	83.4	6.3	44.2	50.5

[a]Sample designations are from Table 20; addition levels are based on oven-dry wood in the pulping reaction.
[b]Total yields are based on oven-dry wood; lignin and carbohydrate yields are based on kappa no. - see Table 11.

The combined Fremy's salt oxidation/Diels-Alder reaction study showed that it was possible to combine oxidation and Diels-Alder reactions into one step. The yield of naphthoquinone from the oxidation of α-methylvanillyl alcohol, however, was less than half of what was achieved through two separate steps. The yield of higher order quinones directly from lignin samples was also quite low, and the oxidized samples showed no activity as pulping catalysts.

Peracetic Acid/Isoprene Reactions

Peracetic acid oxidation was found to produce yields of 2,6-dimethoxy-*p*-benzoquinone which were somewhat lower than those obtained through the use of Fremy's salt. Unlike the Fremy's salt oxidation, however, peracetic acid oxidation involves the use of glacial acetic acid as the reaction medium rather than the use of an almost neutral aqueous reaction mixture. This same acid

medium is used for Diels-Alder reactions of p-benzoquinones with dienes to produce adducts with enhanced ring structures and for the chromic acid oxidation of these adducts to generate fully aromatized naphtho- and anthraquinone compounds. A successful combination of a peracetic acid oxidation with a Diels-Alder reaction therefore seemed likely.

Because in previous work a much higher quinone yield had been obtained from the model compounds than from lignin itself, α-methylsyringyl alcohol and syringaldehyde were examined first. The procedure consisted of a combination of the procedures that were found to be most effective for the individual oxidation and Diels-Alder reaction steps.

In all experiments isoprene was used as the diene. Although isoprene required more vigorous reaction conditions than would have been needed if 2,3-dimethyl-1,3-butadiene had been used, isoprene has more practical importance, and the resulting product, 2,6- and 2,7-dimethylanthraquinone, is a very effective pulping additive. The amount of isoprene used was varied over a fairly wide range.

Unlike the results obtained with Fremy's salt, however, attempts to combine peracetic acid oxidation with Diels-Alder enhancement of the generated quinone were totally without success. The only quinone detected was the benzoquinone resulting from the oxidation step, 2,6-dimethoxy-p-benzoquinone, and this was in very low yield (less than 4%). Remaining peracetic acid or its reaction by-products undoubtedly interfere with the subsequent Diels-Alder reaction of the benzoquinone with the isoprene. Reducing the amount of peracetic acid or increasing the amount of isoprene did not improve the situation. The use of a huge excess of isoprene resulted only in a tarry mass in which no quinone could be detected.

Hydrogen Peroxide/Diene Reactions

A third oxidant which had demonstrated effectiveness in generating quinones from some lignin-related compounds was hydrogen peroxide; the reaction medium for this oxidation is alkaline. An attempt was therefore made to carry out a Diels-Alder reaction in a base. Success might imply some hope of combining a hydrogen peroxide oxidation with a Diels-Alder reaction. Hydrogen peroxide is also much less reactive than peracetic acid with simple dienes.

The experimental procedure used was essentially the same as the procedure that was used earlier to produce 2,6- and 2,7-dimethylanthraquinone, but 1N NaOH was substituted for glacial acetic acid as the reaction medium. Analysis of the chloroform extract of the mixture obtained after reaction, however, showed no naphthoquinone or anthraquinone compounds produced.

The gel-like appearance of the reaction product seemed to indicate some degree of polymerization of the 2,6-dimethoxy-p-benzoquinone starting material. This is in agreement with the findings of Simson[58] and Erdtman[134] who have noted the instability of quinones in basic solutions. Erdtman found that 2,6-dimethoxy-p-benzoquinone is fairly stable toward alkali but that after a prolonged time undergoes polymerization. He also suggested that the high solubility of this quinone in base is probably due to the formation of a complex addition compound. This complex might not be susceptible to a Diels-Alder addition reaction.

Because the Diels-Alder reaction step could not be carried out in base, no further investigation of the possible combination of this reaction with hydrogen peroxide oxidation was attempted. Furthermore, experimental work done by Erdtman[134] has also shown that compared to the dimethoxy compound, methoxy-p-

benzoquinone is highly reactive in base, being immediately polymerized in an alkaline solution. Any success with the use of this quinone is therefore very unlikely.

Summary

For an industrial application, fewer process steps often means greater economic advantage. The combination of oxidation and Diels-Alder reaction has been successfully achieved when Fremy's salt was used as the oxidant. Reaction yields, however, were appreciably lower than when quinones were generated in two separate steps.

Attempts to combine oxidation and Diels-Alder reactions using peracetic acid and hydrogen peroxide were unsuccessful. With peracetic acid, no higher order quinones were generated; with hydrogen peroxide, the Diels-Alder phase of the reaction would not take place. Although further research may lead to more success in this area, at this point the usefulness of combined oxidation/Diels-Alder reactions is questionable.

NITROBENZENE OXIDATION OF LIGNIN TO GENERATE BENZOQUINONE PRECURSORS

The first phase of the experimental work has shown that the best chance for success in generating a pulping catalyst from lignin lies in the generation of p-benzoquinone starting compounds. The use of several oxidative techniques on both lignin and lignin-related compounds has shown that higher p-benzoquinone yields result from the oxidation of simpler lignin-related compounds than from the oxidation of lignin itself. It was noted that syringaldehyde is one of these simpler compounds from which 2,6-dimethoxy-p-benzoquinone can be obtained in fairly good yield.

The technology for the production of simple compounds such as vanillin and syringaldehyde from lignin is fairly well established.[53,137] To gain a better understanding of which pulping processes might give rise to lignins that are most highly susceptible to conversion into these compounds, the nitrobenzene oxidation of several lignin samples was conducted. Nitrobenzene oxidation was introduced as a diagnostic device.[53] The amounts of aromatic aldehydes present in a reaction mixture are determined by the origin and structure of the lignin sample. A mechanism for the oxidation of a lignin unit containing an α-carbonyl group is presented in Fig. 33.

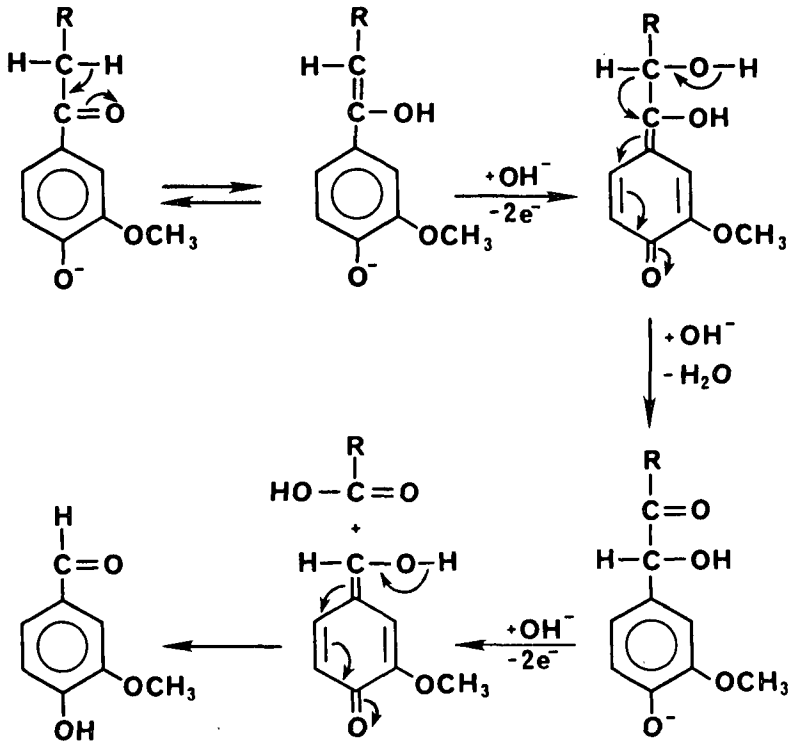


Figure 33. Nitrobenzene oxidation of a lignin unit.[53]

Nitrobenzene oxidations were performed on several lignin samples using a fairly standard procedure[53,128,129] employing 2N NaOH in a stainless-steel pressure vessel at an elevated temperature. Analysis of the reaction mixture

was through gas chromatography using an internal standard technique. The lignin samples used and the results obtained at three different temperatures are presented in Table 23.

Table 23. Nitrobenzene oxidation of various lignin samples.[a]

Sample	Vanillin Yield (%)	Syringaldehyde Yield (%)	Total Yield (%)
Oxidations at 140°C:			
HW Ethanol	5.0	12.9	17.9
SW Soda	10.1	trace	10.1
HW Kraft	3.4	4.8	8.2
SW Kraft	7.9	0.4	8.3
HW Sulfite	5.1	8.9	14.0
SW Sulfite	12.1	trace	12.1
Oxidations at 159°C:			
HW Ethanol	5.8	14.6	20.4
SW Soda	12.9	trace	12.9
HW Kraft	4.6	6.5	11.1
SW Kraft	9.9	0.4	10.3
HW Sulfite	5.6	9.5	15.1
SW Sulfite	15.5	trace	15.5
Oxidations at 179°C:			
HW Ethanol	6.7	17.0	23.7
SW Soda	15.2	trace	15.2
HW Kraft	5.3	7.9	13.2
SW Kraft	13.1	0.6	13.7
HW Sulfite	6.1	10.1	16.2
SW Sulfite	16.5	trace	16.5

[a]Yields are based on the weights of the lignin samples used.

The trend of increasing aldehyde yield with increasing temperature is apparent. Nitrobenzene oxidations reported in the literature generally have been carried out at or below 180°C; it is possible that optimum yields may be obtained at higher temperatures. The high yield obtained from the ethanol

lignin sample, and in particular the high syringaldehyde yield, is notable. Table 23 clearly shows that the acid-catalyzed ethanol pulping process has a good potential for producing a lignin which is highly susceptible to breakdown into compounds which may be subsequently converted into methoxy- and 2,6-dimethoxy-p-benzoquinone.

Nitrobenzene oxidations were also performed on the lmw ethanol lignin sample to see if an increased aldehyde yield might be obtained. Performing duplicate experiments on both this sample and an ethanol lignin sample isolated from a second pulping reaction, gave a good estimate of the amount of error involved in the data. The results are presented in Table 24.

Table 24. Nitrobenzene oxidation of ethanol lignin samples.[a]

Sample	Vanillin Yield (%)	Syringaldehyde Yield (%)	Total Yield (%)
Oxidations at 178°C:			
LMW Ethanol Lignin	3.6	16.7	20.3
	3.7	16.6	20.3
Mean	3.7	16.7	
Std. Dev.	0.1	0.1	
Ethanol Lignin	5.8	16.4	22.2
	5.8	16.7	22.5
Mean	5.8	16.6	
Std. Dev.	0.0	0.2	
Oxidation at 179°C (previous sample):			
Ethanol Lignin	6.7	17.0	23.7
Error between batches:			
Mean	6.3	16.8	
Std. Dev.	0.6	0.3	

[a]Yields are based on the weights of the lignin samples used.

It can be seen that there is good agreement between duplicate samples; the error between batches is somewhat larger. Although the syringaldehyde yields from both the normal and lmw ethanol lignin samples are approximately the same, it is clear that a substantially lower vanillin yield was obtained from the lmw lignin fraction. One possible explanation for this may lie in the lignin isolation procedure. At the beginning of the pulping reaction, the concentration of the HCl was 0.0125M. Prior to the chloroform extraction to obtain the lmw lignin fraction, however, the remaining solution was reduced to approximately one-sixth of its original volume, thereby dropping the pH. This concentration step took several hours and was done at a slightly elevated temperature (generally less than 40°C). These conditions may have been sufficient to cause some acid-condensation type reactions of the guaiacyl lignin units, thus reducing subsequent vanillin yields from the nitrobenzene oxidations. Because of the extra methoxyl group, the syringyl units would not be expected to undergo these reactions to the same extent, and the syringaldehyde yield would not be reduced.

In any case, the data in Table 24 suggest that nothing is gained from the lmw ethanol lignin sample in the way of increased aldehyde yield; therefore, there would also be no increase in quinone yield from the subsequent oxidation of the aldehydes. Overall, all of the lignin generated through acid-catalyzed ethanol pulping should be used as a starting material for the generation of p-benzoquinones.

CONCLUSIONS

Quinone structures of the p-benzoquinone type can be both generated and isolated from lignin and lignin-related compounds. Although o-benzoquinones also are likely generated in lignin, they remain attached in the lignin macromolecule via the propyl side chain. Because they are readily degraded in an alkaline pulping environment, benzoquinones do not function as delignification catalysts.

Both p-benzoquinones and o-benzoquinones, which are generated from lignin and lignin-related compounds, can be converted into higher order quinones, such as naphthoquinones and anthraquinones, through the use of Diels-Alder reactions with 2,3-dimethyl-1,3-butadiene and isoprene. Higher yields of p-benzoquinones are generally obtained from the Diels-Alder reactions. Based on this fact, together with the observation that p-quinones generally exhibit higher delignification catalytic activity, it appears that p-quinones serve better than o-quinones as starting compounds for the generation of pulping catalysts.

Higher p-quinone yields are obtained from simple lignin-related compounds than from lignin itself. For the creation of p-quinones, oxidation with hydrogen peroxide appears useful when compounds contain α-carbonyl groups; potassium nitrosodisulfonate appears useful when compounds contain α-hydroxyl groups; peracetic acid will effectively oxidize compounds containing either type of group. Chemical oxidants show more promise than electrochemistry for generating quinones from lignin and lignin-related compounds.

RECOMMENDATIONS

The potential application of this research in an industrial pulping process is very high. Based on reaction yields that have already been obtained, Fig. 34 shows that using 10% of the lignin present in a typical wood source, enough catalyst can be generated to sustain a pulping process at an addition level of approximately 0.09%. The estimation of this addition level is based on the use of isoprene as a diene and on the assumption that the final Diels-Alder product consists mainly of anthraquinone-related compounds. Because little emphasis was placed on yield optimization in this work, it is likely that the reaction yields can be increased. Any increase would mean that a higher addition level and/or a lower lignin usage can be attained.

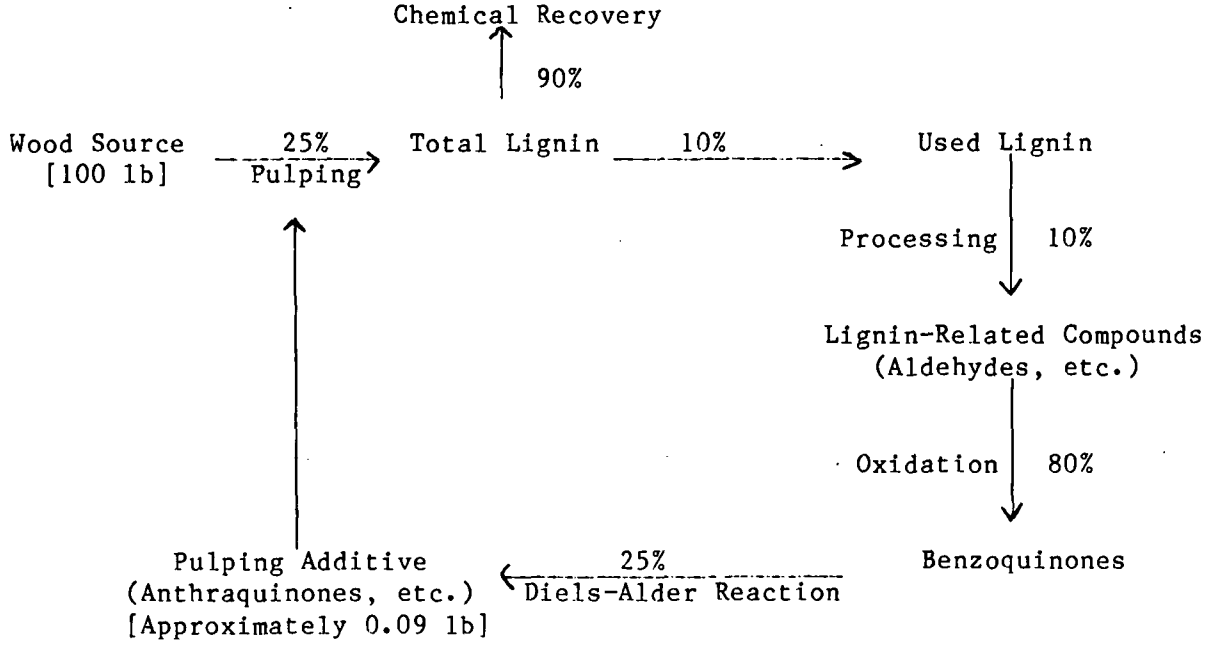


Figure 34. Self-generating catalytic pulping process.

Further work should therefore be carried out toward the creation of a pulping process incorporating a catalyst generation cycle. Toward that end, work must be done to determine optimum conditions for both the generation of

p-benzoquinones from lignin and lignin-related compounds, and for the enhancement of these quinones through Diels-Alder reactions. Oxidative techniques other than those applied in this work might also be investigated. After optimum conditions and yields are established, an economic analysis of the feasibility of the overall process can be conducted. Favorable results of an economic analysis would lead to pilot plant studies and, subsequently, to a full-scale industrial pulping operation.

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APPENDIX I

RETENTION TIMES AND RESPONSE FACTORS OF COMPOUNDS USED

Qualitative determinations of the compositions of the chloroform extracts obtained from the oxidations were largely based on the retention times of compounds on the Hewlett-Packard 530-μm 50% phenylmethyl silicone, fused-silica, open-tubular column that was used. These retention times are presented below along with the response factors (relative to 4-isopropylphenol) used in quantitative analyses.

Table 25. Retention times and response factors of various compounds.

Compound	Molecular Weight	Retention Time (Min)	Response Factor[a]	Error[b]
4-Isopropylphenol	136	1.80		
2-Methoxy-4-vinylphenol	150	2.90		
Methoxy-p-benzoquinone	138	3.20	0.501	0.008
4-Formoxy-2-methoxyphenol	168	4.50		
Methoxyhydroquinone	140	4.70	0.365	0.007
Vanillin	152	4.80	0.616	0.006
α-Methylvanillyl Alcohol	168	5.40	0.560	0.029
4-Acetoxy-2-methoxyphenol	182	5.70		
Acetovanillone	166	6.05	0.685	0.029
2,6-Dimethoxy-4-vinylphenol	180	6.95		
Vanillic Acid	168	7.15	0.304	0.014
2,6-Dimethoxy-p-benzoquinone	168	9.10	0.378	0.033
2,6-Dimethoxyhydroquinone	170	9.70		
Syringaldehyde	182	9.75	0.519	0.015
α-Methylsyringyl Alcohol	198	10.35	0.503	0.044
4-Acetoxy-2,6-dimethoxyphenol	212	10.70		
Acetosyringone	196	10.90	0.576	0.021
Syringic Acid	198	12.55	0.300	0.020
2-Methoxy-6- & 7-methyl-1,4-naphthoquinone	202	14.60	0.824	0.069
2-Methoxy-6,7-dimethyl-1,4-naphthoquinone	216	17.60	0.649	0.077
2,6- & 2,7-Dimethyl-anthraquinone	236	19.55	0.979	0.065

[a]Relative to 4-isopropylphenol.

[b]Standard error of estimate of ratio of compound to internal standard GC peak area as determined by linear regression analysis.

The temperature program that was used in the analyses was 140 to 230° at 5°/min, 230 to 280° at 10°/min and 5 min at 280°C; He flow rate was approximately 8 mL/min. The response factors were determined through linear regression analysis of data values obtained by plotting the ratio of compound to internal standard GC peak area vs. the actual mole ratio of compound to internal standard. The standard error of the estimate of the ratio of compound to internal standard GC peak area for each compound, as determined by this analysis, is included in the table.

APPENDIX II

ANALYTICAL PROCEDURES FOR DETERMINATION OF EXTENT OF QUINONE GENERATION

Although not used extensively in the experimental work, two procedures were developed for the determination of the extent of quinone generation in lignin and lignin-related compounds. These involved the use of an iodometric titration, and the use of an acetylation/aminolysis technique.

IODOMETRIC TITRATION

Iodometric titration is a well-known technique for the determination of species that are capable of quantitatively oxidizing the iodide ion to elemental iodine.[138] The amount of iodine liberated can be measured through titration with sodium thiosulfate. This technique has been used for the determination of benzoquinone,[139] and is used in the determination of kappa number.[131] Although it was found useful for determining both p- and o-benzoquinones, the technique could not be used for determining other types of quinones, including those found in lignin.

The compound being tested (50.0 mg) was dissolved in an appropriate amount of solvent (typically 2.5 mL). Dilute H_2SO_4 (4N, 7.5 mL) was then added; this was followed by the addition of 2.5 mL of 1N KI solution. The I_2 liberated was titrated using 0.1N $Na_2S_2O_3$ solution (Acculute). A few drops of starch indicator solution were added just before the end-point. Results obtained are summarized in Table 26. In this table the quinone determination by iodometric titration is expressed as a percentage of the actual amount of quinone used.

Iodometric titration appears to be a very useful method for determining p-benzoquinones. Better results were obtained using acetone as a solvent than

ethylene glycol monomethyl ether. Although not extensively tested, dimethyl sulfoxide also gave excellent results. Iodometric titration can probably also be used to accurately determine simple o-benzoquinones. Because 4-methyl-o-benzoquinone is very reactive, the sample used was very likely not 100% pure; a purity of 85% is certainly possible, and this could be what is reflected in the determination presented.

Table 26. Quinone determination by iodometric titration.

Compound	Percentage of Quinone Detected		
	Acetone	EGME[a]	DMSO[b]
Methoxy-p-benzoquinone	98	93	99
2,6-Dimethoxy-p-benzoquinone	99	97	
4-Methyl-o-benzoquinone	83	76	

[a]Ethylene glycol monomethyl ether.
[b]Dimethyl sulfoxide.

ACETYLATION/AMINOLYSIS

The combination of acetylation followed by aminolysis with pyrrolidine has been used to accurately determine the phenolic hydroxyl content of various lignin samples.[140] Phenolic acetyl groups react very rapidly with pyrrolidine to generate N-acetylpyrrolidine which may be detected by GC analysis. Although nonphenolic acetyl groups also react, the rate is much slower. Therefore, by plotting a graph of N-acetylpyrrolidine generated vs. time and extrapolating to zero time, the amount of N-acetylpyrrolidine from the phenolic groups alone can be determined.

This technique was adopted for use in determining the extent of quinone generation in an oxidized lignin sample by comparing the phenolic hydroxyl

content of the sample before and after oxidation. The change in phenolic hydroxyl content may be taken as a measure of the conversion of hydroxyl groups to carbonyl (quinone) groups.

Both acetylation and reductive acetylation (in which carbonyl groups are first reduced to hydroxyl groups) must be used on a sample, because (1) oxidation may convert phenolic hydroxyl groups into nonquinone structures which cannot be acetylated, or (2) demethylation without oxidation can occur. In the first case, acetylation alone will indicate a quinone content that is too high, and reductive acetylation will indicate a quinone content that is too low. In the second case, the situation is reversed. As the following argument shows, the correct quinone content is the average of the values obtained through the two acetylation techniques:

Suppose that initially there are 100 phenolic hydroxyl units and that after oxidation there are x quinone units (2 carbonyl groups on each), y nonquinone structures which can be neither acetylated directly nor reduced and acetylated, and z catechol units (2 hydroxyl groups on each). Acetylation will indicate:

$$100 - [100 - (x + y + z) + 2z] = x + y - z \text{ quinone units} \qquad (28)$$

Reductive acetylation will indicate:

$$[100 - (x + y + z) + 2x + 2z] - 100 = x - y + z \text{ quinone units} \qquad (29)$$

Thus, the average of these two values is the correct number of quinone units.

The relative magnitude of the values obtained through acetylation and reductive acetylation should indicate which type of reaction (oxidation into nonquinone structures or demethylation without oxidation) predominated during

oxidation. Comparison of phenolic hydroxyl contents of the unoxidized lignin obtained through the two techniques should indicate the degree to which the lignin already contains quinone units. Generally, it would be expected that there would not be a significant difference between the two values.

The acetylation/aminolysis procedure was used to evaluate a sodium periodate-oxidized lignin sample.[33] To obtain the periodate lignin, 0.56 g of soda lignin was first dissolved in 60 mL of 90% acetic acid and cooled to approximately 2°C. A sodium periodate solution consisting of 20 mL of 0.14M $NaIO_4$ in 60% acetic acid was also cooled to approximately 2° and then added to the lignin solution. Following stirring for 4 min, 20 mL ethylene glycol (also at 2°) was added to consume any unreacted $NaIO_4$. After stirring an additional 2 min, the mixture was poured into 400 mL of cold (2°) distilled water. The precipitated lignin was centrifuged for 30 min and collected by decanting the supernatant liquid. To prevent loss of product, the supernatant was filtered through a fine fritted-glass Buchner funnel. The lignin was then washed four times by dispersing in cold water, collected by centrifuging and filtering the supernatant, and freeze dried.

Lignin samples were acetylated[33] by first dissolving 0.50 g of lignin in 2.50 mL of dry pyridine in a 50-mL round-bottom flask; acetic anhydride (1.25 mL) was then added. The flask was flushed with nitrogen, stoppered, and then stirred at room temperature for 24 hours. Following reaction, the mixture was filtered through a fine fritted-glass Buchner funnel and hydrolyzed over approximately 100 mL of crushed ice. The precipitated lignin was centrifuged, washed, and freeze dried as described above for periodate lignin except that the second wash was with 0.01N HCl.

Reductive acetylation[33] was carried out by first dissolving 0.50 g of lignin in 2.50 mL of dry pyridine in a 50-mL round-bottom flask equipped with a reflux condenser connected to a $CaCl_2$ drying tube; zinc dust (0.125 g, 25% of the weight of the lignin) and acetic anhydride (1.25 mL) were then added. The flask was then placed in a 100°C glycerol bath for 1 hour with stirring. Following reaction, the mixture was cooled to room temperature and filtered through a fine fritted-glass Buchner funnel; any remaining Zn dust was washed with approximately 10 mL of a 1:1 mixture of acetic acid and pyridine. The filtrate was hydrolyzed over crushed ice, and the precipitated lignin was isolated as described above.

The aminolysis reaction[140] was carried out by adding 10.0 mg of acetylated lignin to 0.5 mL of p-dioxane in an 8-mL vial equipped with a small stirring bar. Distilled pyrrolidine (0.5 mL) containing N-formylpyrrolidine (3.3 mg) as an internal standard for GC analysis was then added.

Following the addition of the pyrrolidine in the aminolysis reaction, a sample was immediately injected into the GC; samples were analyzed at 10-min intervals. A Hewlett-Packard 530-μm methyl silicone, fused-silica column quantitatively separated N-formyl- and N-acetylpyrrolidine. The GC was set at 80°C for 5.5 min; He flow rate was 6 mL/min. Because the pyrrolidine compounds appeared to gradually build up on the column, a cleaning run, using p-dioxane only, was performed between analyses. The phenolic acetyl content was calculated by graphing mmoles N-acetylpyrrolidine formed per gram of acetylated lignin vs. reaction time and extrapolating the kinetic curve to zero time. A typical example of the type of graph obtained is shown in Fig. 35.

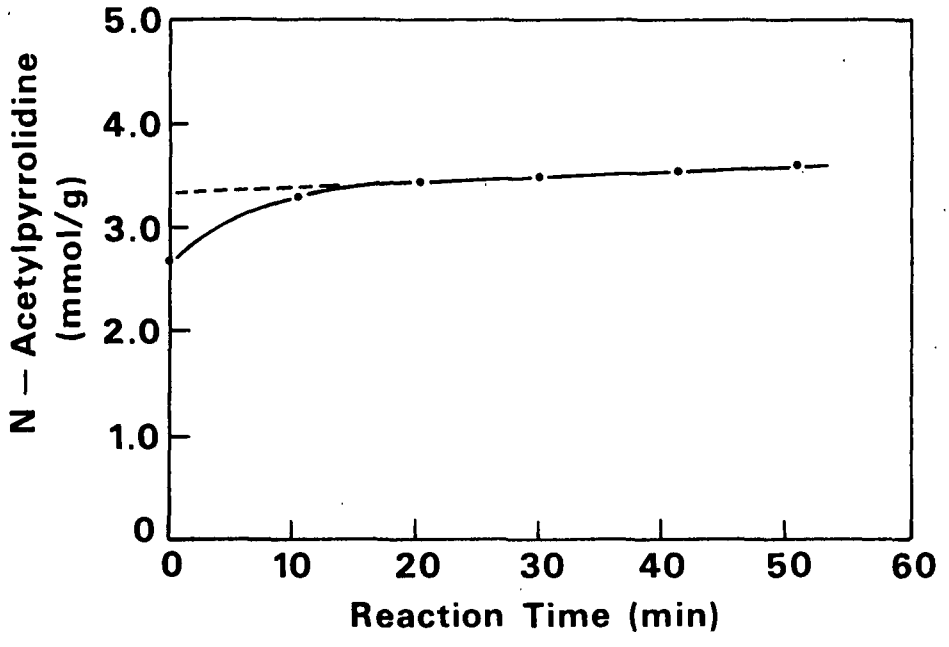

Figure 35. Kinetic curve for the reaction of pyrrolidine with acetylated periodate lignin.

Results of an analysis of the quinone content of a periodate lignin sample are presented in Table 27. The value given in the table for the acetylated lignin is the mean value of two determinations; since the standard deviation for these two values was 0.23, the difference between the values for the acetylated and the reduced, acetylated samples is not significant. One possible source of error in this procedure lies in the fact that oxidized, acetylated lignin samples do not appear to be completely soluble in p-dioxane.

Table 27. Quinone determination by acetylation/aminolysis.

Lignin Sample	Phenolic Hydroxyl Content (mmol/g lignin)
Acetylated	3.57
Oxidized, Acetylated	3.33
Change	-0.24 (-7%)
Reductively Acetylated	3.67
Oxidized, Red. Acetylated	4.04
Change	+0.37 (10%)

It should also be pointed out that slight adjustments in the results must be made for differences in molecular weight among the lignin preparations used. With these adjustments (assuming the average molecular weight of a phenyl propane unit in the original lignin to be 180, 1.2 hydroxyl groups per C_9 unit, and 0.1 carbonyl groups per C_9 unit), Table 27 indicates an increase in quinone content of approximately 11%.